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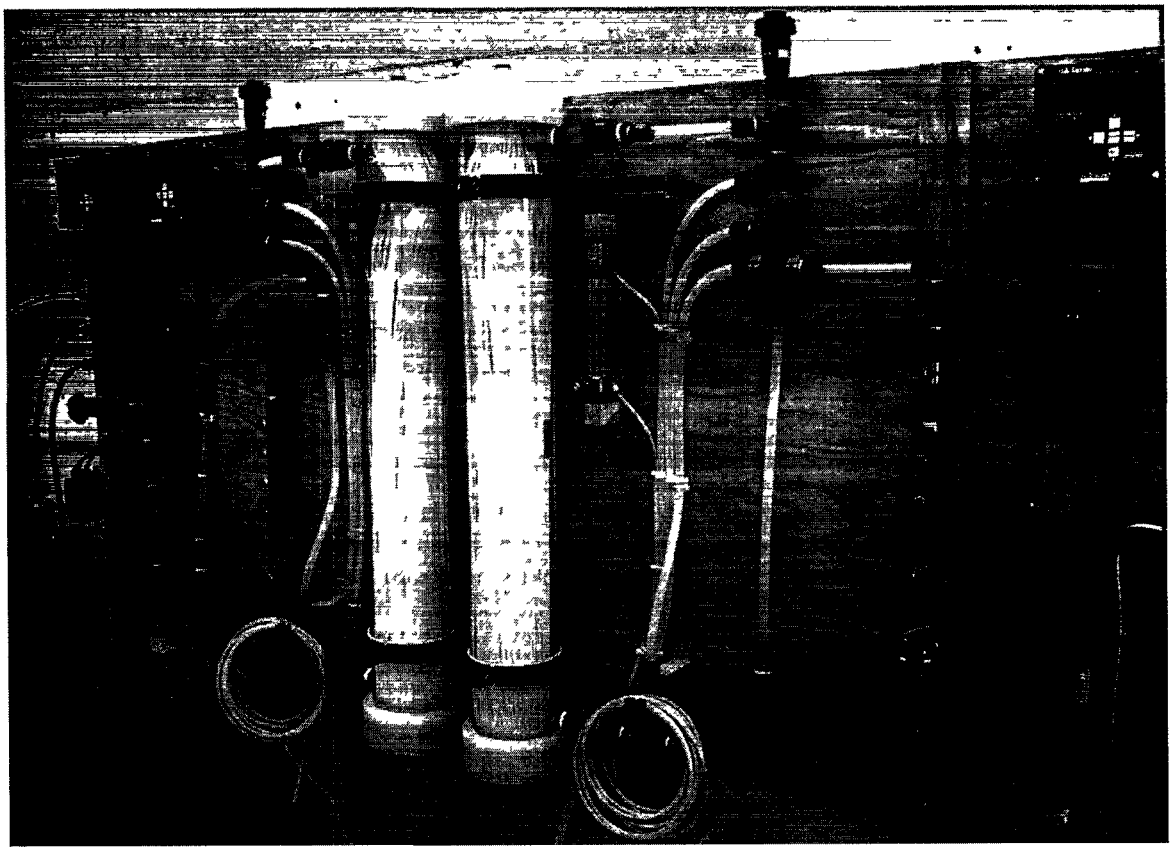

Progress Report No. 4

Application of Bioreactor Systems to Low-Concentration Perchlorate-Contaminated Water

April 2003

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Northwestern University

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on

Application of Bioreactor Systems to Low-Concentration Perchlorate-Contaminated Water

April 2003

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Table of Contents

Section Name **Page Number**

LIST OF TABLES

LIST OF FIGURES

List of Acronyms and Abbreviations

°C	Degrees Celsius
atm	Atmosphere
CaDHS	California Department of Health Services
CCL	Contaminant Candidate List
Cl^-	Chloride
ClO_2^-	Chlorite
ClO_3^-	Chlorate
ClO_4^-	Perchlorate
cm	Centimeter
CSTR	Continuous flow stirred tank reactor
DO	Dissolved (aqueous) oxygen
DW	Dry weight
gpm	Gallons per minute
MBfR	Hydrogen-fed hollow-fiber membrane biofilm reactor
HRT	Hydraulic residence time
IC	Ion chromatograph
L	Liter
M	Molar
MDL	Method Detection Limit
MDTC	Membrane-covered dynamic thermal conductivity
mg/L	Milligram per liter
min	Minute
mL	Milliliter
mM	Millimolar
MRL	Method Report Limit
µg/L	Microgram per liter
µL	Microliter
ND	Non Detect
NH_4ClO_4	Ammonium perchlorate
nm	Nanometer
NO_2^-	Nitrite
NO_3^-	Nitrate
NWU	Northwestern University
O_2	Oxygen
PCR	Polymerase chain reaction
QAPP	Quality Assurance Project Plan
R	Recycle ratio
t	Time
t_R	Theoretical hydraulic residence time
UCMR	Unregulated Contaminants Monitoring Rule
USEPA	United States Environmental Protection Agency

Chapter 1 - Introduction

Since the discovery of perchlorate contamination in a number of California groundwaters in 1997, it has been detected in many other locations across the country. The United States Environmental Protection Agency (USEPA) estimates that groundwaters in 40 states have the potential to be contaminated with perchlorate, and has confirmed perchlorate releases in approximately half of them (EPA 2002). Perchlorate (ClO_4^-) appears to be linked to the historical manufacturing, usage, or processing of ammonium perchlorate (NH_4ClO_4), a solid rocket fuel. In March 1998, the USEPA formally added perchlorate to the drinking water contaminant candidate list (CCL) (Perciasepe, 1998). Its monitoring in drinking water supplies was mandated in 1999 under the Unregulated Contaminants Monitoring Rule (UCMR) (Browner, 1999). The primary concerns over perchlorate toxicity are based on its interference of iodide uptake by the thyroid gland, as well as the related possible carcinogenic, developmental, reproductive, and immunotoxic effects resulting from this interference.

As a collaborative effort between MWH and Northwestern University, the application of bioreactor systems to low-concentration perchlorate-contaminated water is being investigated. The first phase of the project, focused on bench-scale testing of a novel hydrogen-fed hollow-fiber membrane biofilm reactor (MBfR), has been completed. It was discovered that a bench-scale MBfR was effective in reducing 50 to 1000 µg/L perchlorate to below the previous California Department of Public Health Services Advisory Action Level of 18-µg/L. The mechanisms by which this reduction occurred, however, were not entirely clear, and the kinetics were not well defined. Additionally, when the reactor was switched from a tap water-based medium to a minimal medium based on RO water, the perchlorate reducing efficiency progressively decreased to almost zero over 6 months even though nitrate reduction was not affected. Therefore, the ecology of the reactor was suspected to play an important role in perchlorate removal.

1.1 PRIMARY PROJECT OBJECTIVES

Expanding on the first phase of the project, Phase II has focused on the implementation of the process at pilot-scale. The Phase II pilot-testing program has three main objectives:

1. Determine the long-term performance of pilot-scale MBfRs for perchlorate removal. A total of three systems will be evaluated: 1) two reactors in series, 2) single reactor (same membrane fiber as two reactors in series system, but different membrane module design), and 3) single reactor (different membrane and module design as compared to #2). Effluent water quality will be established in terms of major anions and intermediate by-products. Operational reliability will be evaluated in terms of operation and maintenance requirements.

2. Evaluate and determine system operational and design parameters that affect the biodegradation of perchlorate. Some of the critical parameters that will be evaluated will include nitrate concentration, hydrogen consumption, membrane surface area, and membrane module design. Insufficient information exists that describes whether perchlorate degradation can occur in the absence of nitrate. The two-reactors-in-series pilot plant design will enable the system to be operated such that the nitrate concentration in portions of the bioreactor can be controlled, and presumably eliminated. The hydrogen consumption rate will also be monitored. The bench-scale system in Phase I was not large enough to reliably measure hydrogen consumption rates or determine the minimum membrane surface area required. Hydrogen consumption will be monitored through the hydrogen feed rate and the dissolved hydrogen concentration in the bulk liquid.

3. Evaluate reactor design. The three different reactor designs identified in the first primary objective will be evaluated. The two single reactor designs will build upon the knowledge gained through the operation of the two-reactors-in-series system. Specific attention during the design of the two single reactor systems will be given to the recycle flow requirements within the reactors, cleaning, fiber breakage and complexity. Characteristics of the fibers will be assessed before and after long-term operation of the systems.

4. Evaluate the unit operations downstream of the MBfR that would be necessary for the production of potable quality water. An aeration tank and a biologically active media filter will be evaluated to aerobically degrade any residual hydrogen from the effluent water, increase the dissolved oxygen levels from an anoxic environment, capture biomass that detaches from the membranes, and degrade biodegradable organic carbon (BDOC), thus providing a biologically stable water before it might enter a distribution system.

1.2 SECONDARY PROJECT OBJECTIVES

Secondary objectives that will be addressed during this phase of the project include:

- Ascertain those issues that might need to be addressed before regulatory approval of the process for potable water production could be granted;
- Develop preliminary design criteria for a full-scale system and evaluate costs;
- Identify full-scale operational and maintenance issues;
- Continue bench-scale testing for evaluating kinetics of hydrogen-oxidizing, perchlorate-reducing bacteria and of "co-metabolic" perchlorate reduction by denitrifying bacteria;
- Explore the microbial ecology of the MBfR, how it affects perchlorate reduction and what by-products may be produced during perchlorate reduction.

Chapter 2– Materials and Methods

To accomplish the objectives of this research, many analytical methods and various experimental systems and procedures are being employed. The analytical methods are being used to assess the water quality and quantify the performance of the experimental systems. Experimental procedures are being used to operationally characterize the microbial ecology of mixed cultures and spatial relationships within the biofilms. During the course of the research, the methods and procedures are subjected to stringent quality control to identify variability or error within the analytical and experimental results.

2.1 PILOT PLANT

Designed, constructed and installed in MWH's Mobile Water Treatment Pilot Trailer during the initial periods of this project, the pilot plant is now located in La Puente in southern California. This site is owned and operated by the La Puente Valley County Water District. The site has an active groundwater well that employs a full-scale 2,500 gpm Calgon Carbon Corporation ISEP ion-exchange system for the removal of perchlorate. A photo of the exterior of the trailer and system feed tank is shown in Figure 2-1.

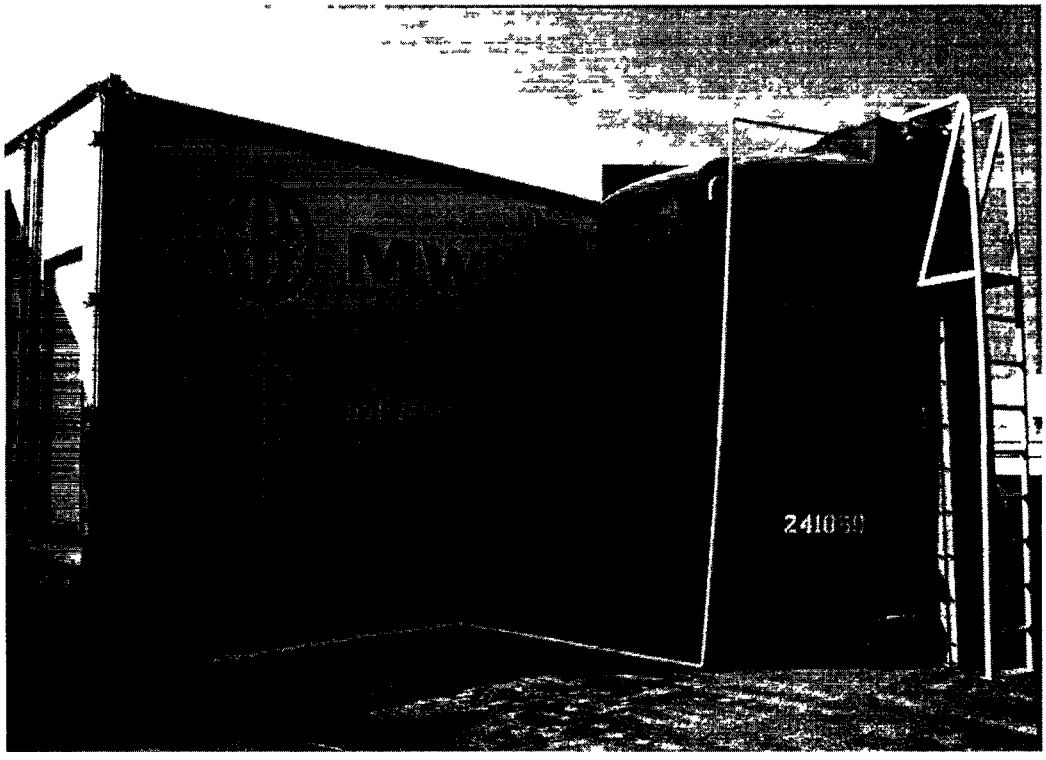


Figure 2-1
Pilot Plant Trailer and Influent Reservoir

2.1.1 Process Description

Figure 2-2 shows a picture of the pilot plant. The pilot plant includes various novel hydrogen-fed hollow fiber membrane biofilm reactors (MBfRs), followed by an aeration basin and a media filter. The membrane biofilm reactors (Mitsubishi, Japan; Membrana, Charlotte, NC) contain fibers potted either at one or both ends of a cylindrical reactor. The water passing through each individual reactor can be recirculated to control the linear velocity through the modules. For each system, an air scour is also periodically applied to the MBfRs to help keep the fibers from sticking together and reduce the clumping of biomass on the membrane surface.

Hydrogen is fed to one end of the reactors, filling the inside of the fibers and diffusing through the membranes to serve as an electron donor for the biofilm. The hydrogen pressure is maintained below the bubble-point of the membrane, eliminating the formation of a hydrogen atmosphere within the bioreactors. The perchlorate-contaminated water is then treated as it passes along the biofilm on the outside of the fibers.

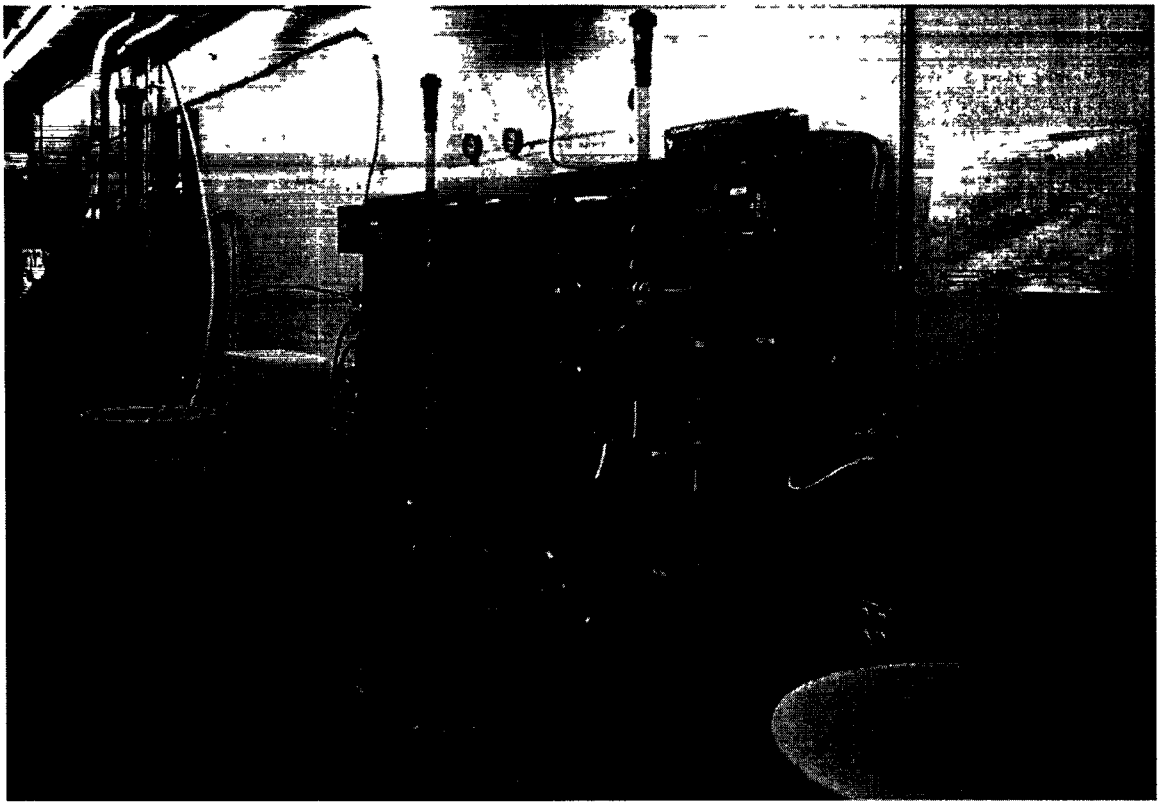


Figure 2-2
Biological Perchlorate Reduction Pilot Plant

Following the MBfRs, an aeration process is used to achieve two primary goals: first, it oxygenates the water in preparation for its introduction into a distribution system as a drinking water source; and second, it provides sufficient oxygen for operating the downstream filter in an aerobic biodegradation mode to achieve complete removal of any residual dissolved hydrogen in the water. A process schematic of this system is shown in Figure 2-3 to help illustrate some of these details.

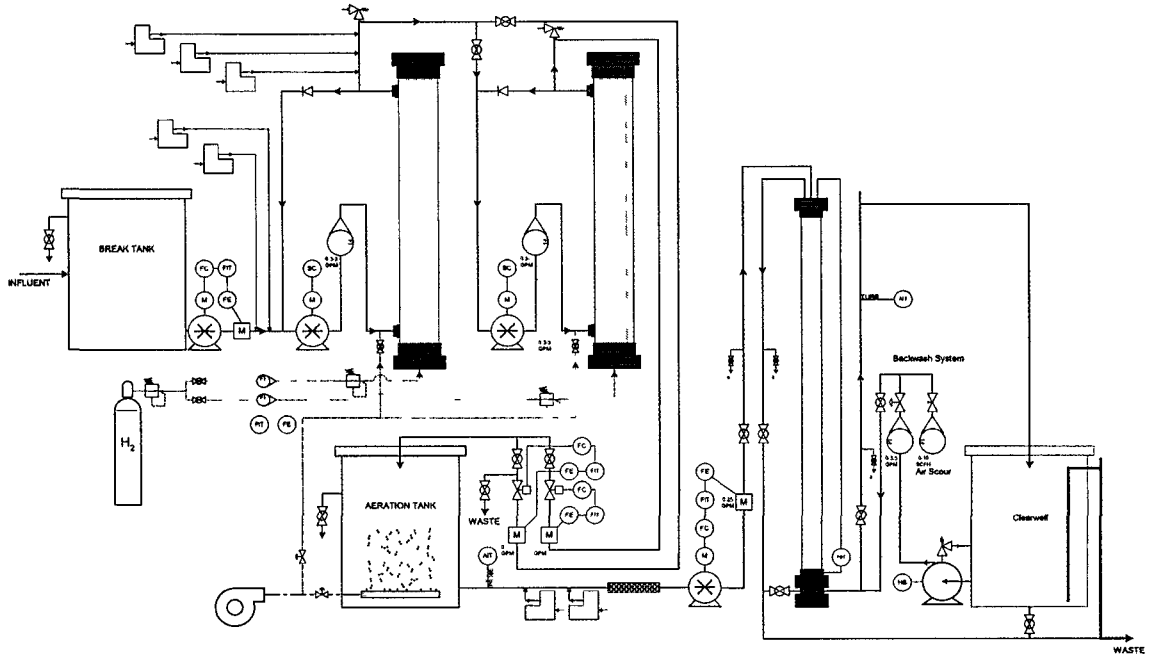


Figure 2-3
Biological Perchlorate Reduction Pilot Plant Process Schematic

2.1.2 Process Sampling

The pilot was designed so that samples could be collected from the break tank (influent water), influent and effluent of each bioreactor, aeration tank effluent, and media filter effluent. Sampling sites were selected to provide a complete analysis of a variety of processes used in this study. The frequency of sample collection was based on operational conditions and historical performance.

2.1.3 Reactor Fiber Repair

Compromised fibers detected during pilot testing are repaired according to the following procedure. First all liquid connections to the MBfR module with the compromised fiber are disconnected and the entire module is removed from the system panel. The potted fiber ends are then exposed by removing the two module end caps used to contain the gaseous hydrogen. The module, now with end caps removed, is mounted back to the

system panel and all liquid connections are reattached. To identify which fiber within the potting is compromised, the module is filled with water until a bead of water is observed coming out of each end of the compromised fiber. The identified fiber of interest is then marked with a syringe needle for further repair.

To repair the identified fiber, a fine tipped soldering iron and extra membrane material are required. As outlined by the reactor manufacturer, the soldering iron is used to melt a 1-mm deep groove surrounding the compromised fiber (marked by the syringe needle) in its appropriate fiber bundle. A small amount of membrane fiber material is then melted to seal the end of the compromised fiber, as shown in Figure 2-4. The aforementioned groove is used to contain the melted membrane material, and prevent it from spreading and blocking uncompromised fibers.

Once both ends of the compromised fiber are repaired, the module is pressurized with water and the repaired ends are checked for liquid leaks. The end caps are then reattached to the module and a gas leak test was performed on the module by pressurizing the end caps and lumens of the fibers with compressed air. If no air bubbles are observed, all liquid and gas connections are reconnected and the MBfR system is returned to service.

Figure 2-4
Repair using Soldering Iron and Membrane Material

2.1.4 Influent Water Quality

Selected parameters have been monitored in the influent water quality. The influent groundwater has been generally stable for most of the parameters monitored, as summarized in Table 2-1. The alkalinity, temperature and pH of the water during this same period are shown in Figure 2-5. The concentrations of other selected water quality parameters (perchlorate, sulfate, nitrate) are displayed in Figure 2-6. Apparent from this figure, there has been a decreasing trend in the perchlorate concentration since the beginning of the study. While the well from which the water is drawn from does not operate on a continuous basis, it does not appear to be affecting the water quality.

Table 2-1
Influent Water Quality Summary

Parameter	Unit	Median	Average	Standard Deviation	Range
Temperature	°C	19	18.6	1.1	15.9 – 20.5
Turbidity	NTU	0.4	0.4	0.08	0.31 - 0.43
pH		8.1	8.1	0.11	7.68 - 8.3
Total Alkalinity	mg $CaCO_3$/L	173	18168	28	162- 205
Conductivity	µS	491	491.0	2.8	489 - 493
Perchlorate	µg/L	52	52	2.8	46 - 56
Nitrate as N	mg/L	5.7	5.9	0.42	5.2 – 6.6
Sulfate	mg/L	37.1	36.1	1.7	33 - 37.8

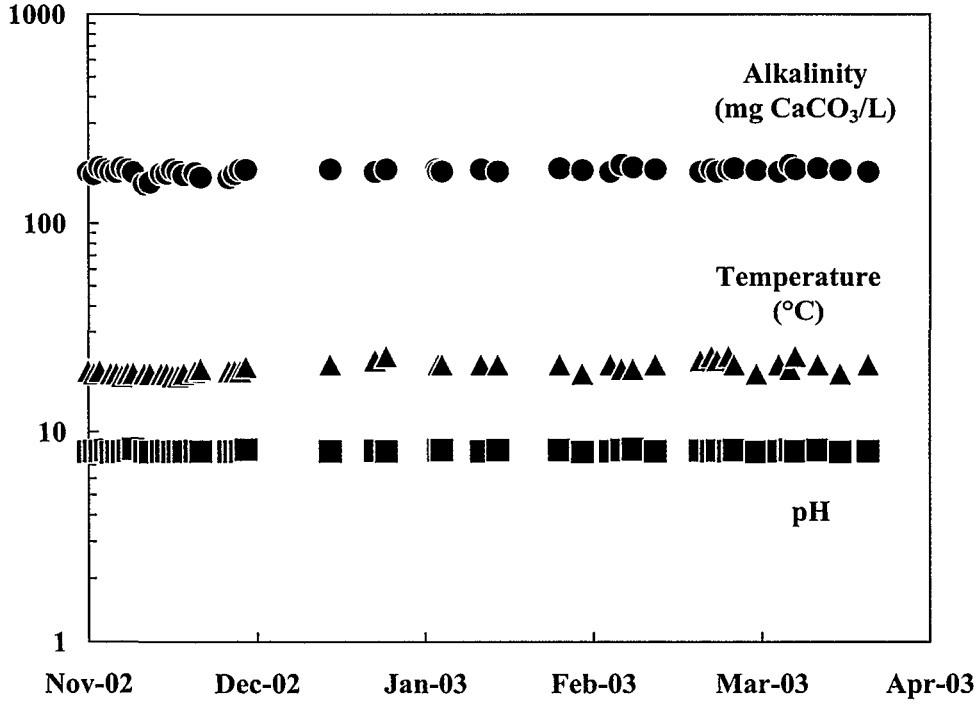


Figure 2-5
General Influent Water Quality (Alkalinity, Temperature, pH)

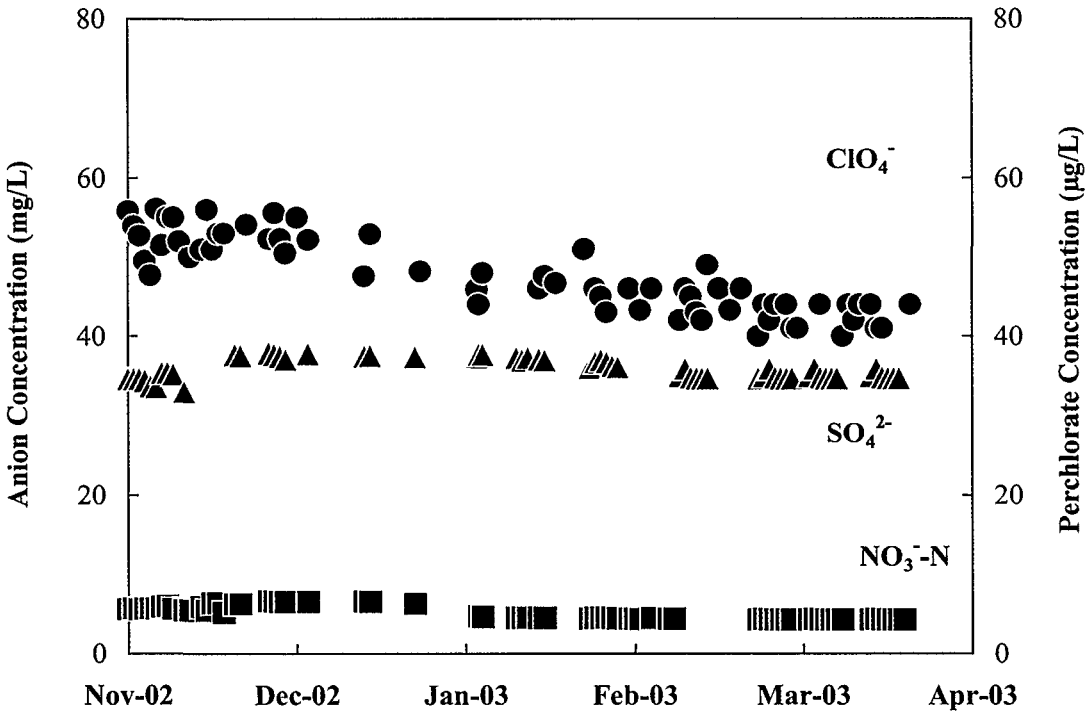


Figure 2-6
Selected Influent Water Quality Parameters

2.2 MICROBIAL ECOLOGY CHARACTERIZATION

The activities focused on the characterization of perchlorate reducing microbial ecology during this period were centered about two tasks: identification and characterization of pure cultures of perchlorate-reducing bacteria, and studies on MBfR microbial ecology. The steps used to carry out these tasks are described below.

2.2.1 Identification and Characterization of Perchlorate-Reducing Bacteria

To isolate strains of perchlorate-reducing bacteria from the pilot-scale MBfR, serum bottles containing growth medium (Table 2-2) with hydrogen and perchlorate were inoculated with biofilm from the pilot-scale system. After growth was observed, the cultures were plated on R2A agar. Colonies were picked and grown again with hydrogen and perchlorate to confirm their perchlorate-reducing ability. Plating was repeated to verify purity.

Batch kinetic studies were carried out using 1-liter bottles or 160-mL serum bottles, capped with a thick, butyl-rubber stoppers. Growth medium was amended with perchlorate, chlorate, or nitrate and adjusted to a final pH of 7. Bottles were filled with sterile media and vacuum degassed and filled with a gas mixture of 95 percent H_2 and 5

percent CO_2, and inoculated with bacteria grown at exponential growth phase. Biomass was determined by correlating absorbance at 600 nm to dry weight measurements. The experiments were run at 22°C on a shaker table at 200 rpm.

Table 2-2
Growth Medium for Batch Studies

Component	Concentration (mg/L)
KH_2PO_4	1.386
Na_2HPO_4	0.849
$(NH_4)_2SO_4$	100
$MgSO_4.7H_2O$	200
$CaCl_2.2H_2O$	1
$FeSO_4.7H_2O$	1
$ZnSO_4.7H_2O$	0.1
$MnCl_2.4H_2O$	0.03
H_3BO_3	0.3
$CoCl_2.6H_2O$	0.2
$CuCl_2.2H_2O$	0.01
$NiCl_2.6H_2O$	0.01
$Na_2MoO_4.2H_2O$	0.03
Na_2SeO_3	0.03

2.2.2 Bench-Scale Microbial Ecology Reactors

To track the development of the microbial ecology five bench-scale MBfRs were constructed. Four reactors were operated to steady state with 8 mg/L oxygen plus 5 mg-N/L nitrate. After reaching steady state, biofilm was sampled for molecular studies. Subsequently, perchlorate was fed in varying concentrations to three reactors, and a fourth remained with only nitrate. A fifth was allowed to reach steady state with oxygen alone, and then was also fed perchlorate.

2.2.2.1 Microbial Ecology Reactor Configuration

The reactor configuration is shown in Figure 2-7 and described in Table 2-3. Each reactor is a loop made from glass tubes connected with Norprene tubing and plastic "tee" fittings. One glass tube contains a bundle of 32 hollow-fiber membranes collected into a manifold at the bottom end and remained free at the top end. The manifold is supplied with 100% hydrogen gas, and the top ends of the fibers are sealed.

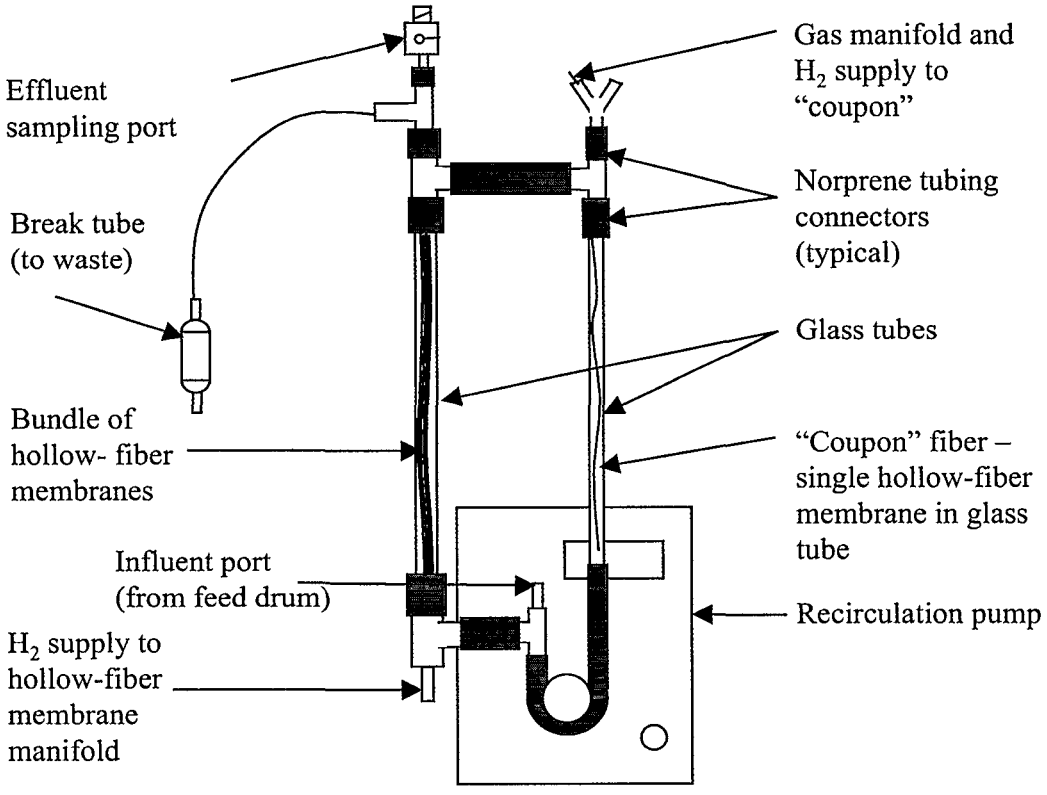


Figure 2-7
MBfR Configuration

Table 2-3
Nitrate and Oxygen Reactor Characteristics

	Units	Main Tube	Return Tube	Total
Tube inside diameter	cm	0.6	0.5	-
No. of hollow fibers		32	1	33
Cross-sectional area fibers	cm^2	0.019704	0.000616	0.02032
Feed rate	mL/min	-	-	1
Recirculation rate	mL/min	-	-	150
Net cross sectional area	cm^2	0.26	0.20	-
Fiber surface area	cm^2	70.37	2.20	72.57
Liquid velocity	cm/min	570.3	766.3	-
Average detention time	min	-	-	23.9

A manifold pump supplied 1 mL/min from a common medium drum to the four nitrate reactors. Varying perchlorate concentrations were added from sterile stocks with 0, 5, 50, and 500 mg/L perchlorate using a second manifold pump at 0.02 mL/min. Final perchlorate concentrations were 0, 0.1, 1, and 10 mg/L. A schematic of the setup for the four nitrate reactors is provided in Figure 2-8. The nitrate media was prepared in a 20-L batch drum and filter-sterilized into a second, sterile feed drum. The setup for the oxygen

reactor (not shown in Figure 2-8 but shown in Figure 2-9) was the same, except the feed came from single 8-L bottle containing nitrate and 1 mg/L perchlorate. The media fed to each of these nitrate and oxygen reactors is presented in Table 2-4.

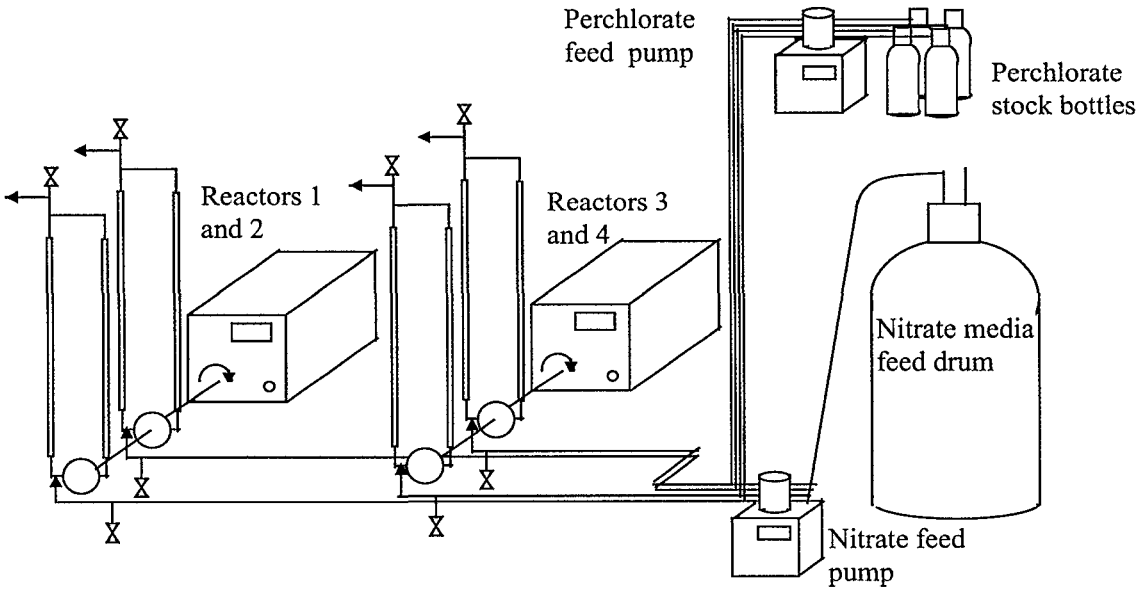


Figure 2-8
Setup for Reactors 1 to 4

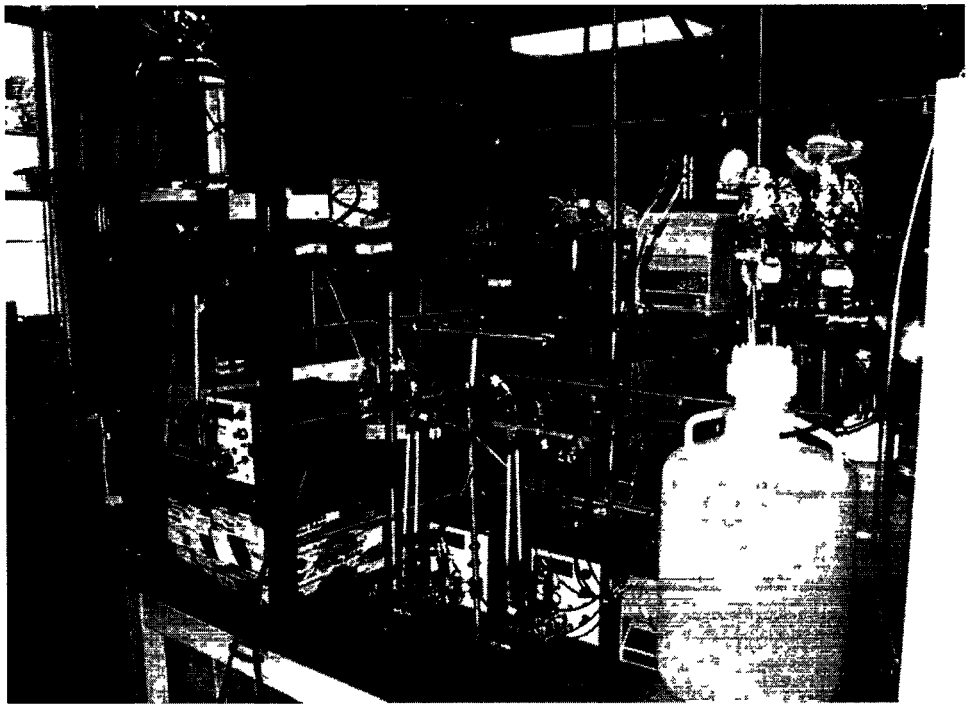


Figure 2-9
Bench-Scale Reactors 1 through 5

Table 2-4
Bench-Scale MBfR Reactor Media

Component	Nitrate Medium (mg/L)	Oxygen Medium (mg/L)
KH_2PO_4	128	29
Na_2HPO_4	434	538
NO_3^- (as N)	5	-
$(NH_4)_2SO_4$	-	10
$MgSO_4.7H_2O$	200	200
$CaCl_2.2H_2O$	1	1
$FeSO_4.7H_2O$	1	1
$ZnSO_4.7H_2O$	0.1	0.1
$MnCl_2.4H_2O$	0.03	0.03
H_3BO_3	0.3	0.3
$CoCl_2.6H_2O$	0.2	0.2
$CuCl_2.2H_2O$	0.01	0.01
$NiCl_2.6H_2O$	0.01	0.01
$Na_2MoO_4.2H_2O$	0.03	0.03
Na_2SeO_3	0.03	0.03

2.2.2.2 Reactor Inoculation and Operation

The reactors were inoculated using biofilm from the pilot-scale plant. At the time of the biofilm collection on March 18, 2002, the first module removed 81 percent of the influent nitrate and 52 percent influent perchlorate, while the second module removed 99 percent of the influent nitrate and 49 percent of the perchlorate. Biofilm from each module was shipped to Northwestern University overnight in a cooler at 4°C. Once received, the samples were mixed and preserved in 25 percent glycerol at –80°C.

Prior to inoculation, the reactors were sterilized by pumping in at least 3 reactor volumes of 0.6 percent hydrogen peroxide in deionized water into each reactor and allowing the solution to recirculate for 4 hours. For inoculation, the frozen stock was allowed to thaw, washed twice by centrifuging for 15 minutes at 5,000 g and resuspended in 10 mL sterile minimal medium with no electron donor. Then 1.5 mL of the washed biofilm suspension was injected into each of the five reactors. The reactors hydrogen supply was turned on and the reactors were allowed to recirculate for 24 hours to establish a biofilm. Then the influent media was pumped to each reactor at 1 mL/min.

2.3 ANALYTICAL METHODS

Most of the water quality parameters are measured following Standard Methods (1998) or USEPA methods. A summary of analytical procedures used, both approved and other

validated standard methods, is provided below in Table 2-5. A discussion of modified and non-standard methods is also included.

Table 2-5
Summary of Approved or Standard Analytical Procedures

Parameter	Method Number	Method Title	Reference
ClO_4^-	EPA Method 314.0 †	Determination of Low Concentrations of Perchlorate in Drinking Water Using Ion Chromatography	USEPA
	Modified EPA Method 300.1 ††	Analysis of Low Concentrations of Perchlorate in Drinking Water and Groundwater by Ion Chromatography	Dionex
ClO_3^- , ClO_2^-	Modified EPA Method 300.1 †	Determination of Inorganic Anions in Environmental Waters with a Hydroxide-selective column	Jackson *et al.* 2000
	EPA Method 300.1 ††	Determination of Inorganic Anions in Drinking Water by Ion Chromatography	USEPA
Cl^-	Modified EPA Method 300.1 †	Determination of Inorganic Anions in Environmental Waters with a Hydroxide-selective column	Jackson *et al.* 2000
	4500-Cl^- F ††	Chloride-Ion Chromatography Method	Standard Methods (1998)
NO_3^-	Modified EPA Method 300.1 †	Determination of Inorganic Anions in Environmental Waters with a Hydroxide-selective column	Jackson *et al.* 2000
	4500-NO_3-C ††	Ion Chromatographic Method	Standard Methods (1998)

Parameter	Method Number	Method Title	Reference
NO_2^-	Modified EPA Method 300.1 †	Determination of Inorganic Anions in Environmental Waters with a Hydroxide-selective column	Jackson *et al.* 2000
	4500-NO_2-C ††	Ion Chromatographic Method	Standard Methods (1998)
SO_4^{2-}	Modified EPA Method 300.1 ††	Determination of Inorganic Anions in Environmental Waters with a Hydroxide-selective column	Jackson *et al.* 2000
H_2 (g)	Non-standard method	Orbisphere † Trace Analytical ††	
Acetate	4110	Determination of Anions by Ion Chromatography	Standard Methods (1998)
Methanol	Non-standard method		
TOC/DOC	5310C	Persulfate Ultraviolet Method	Standard Methods (1998)
DO	4500-O G.	Membrane Electrode Method	Standard Methods (1998)
Ca^{2+}	Method 200.7	ICP	USEPA
Mg^{2+}	Method 200.6	ICP	USEPA
Total Hardness	2340C	EDTA Titrimetric Method	Standard Methods (1998)
Bicarbonate	4500-CO_2 D.	Calculation	Standard Methods (1998)
NH_3	4500-NH_3 F.	Phenate Method	Standard Methods (1998)
Total Alkalinity	2320B	Titration Method	Standard Methods (1998)
Turbidity	2130B	Nephelometric Method	Standard Methods (1998)
Place counts	9215B	Pour Plate Method	Standard Methods (1998)
Temperature	2550B	Laboratory and Field Methods	Standard Methods (1998)
pH	4500H^+	Electrometric Method	Standard Methods (1998)
Specific Conductivity	2510B	Laboratory Method	Standard Methods (1998)

† Pilot-Scale †† Bench-Scale

2.3.1 Ion Chromatography

Utilizing the latest technology at pilot-scale, perchlorate is analyzed on-site by ion chromatography (IC) using a Dionex DX-320 with conductivity detection using an AS-16 column, a 1000-μL loop, EG-40 eluent generator, and an autosampler as shown in Figure 2-10. EPA Method 314.0 is followed as the analytical protocol. Based on seven injections of a 2-μg/L standard over the period of one week, the MDL has been determined to be 0.7 μg/L. The lowest standard used during calibration is 2 μg/L.

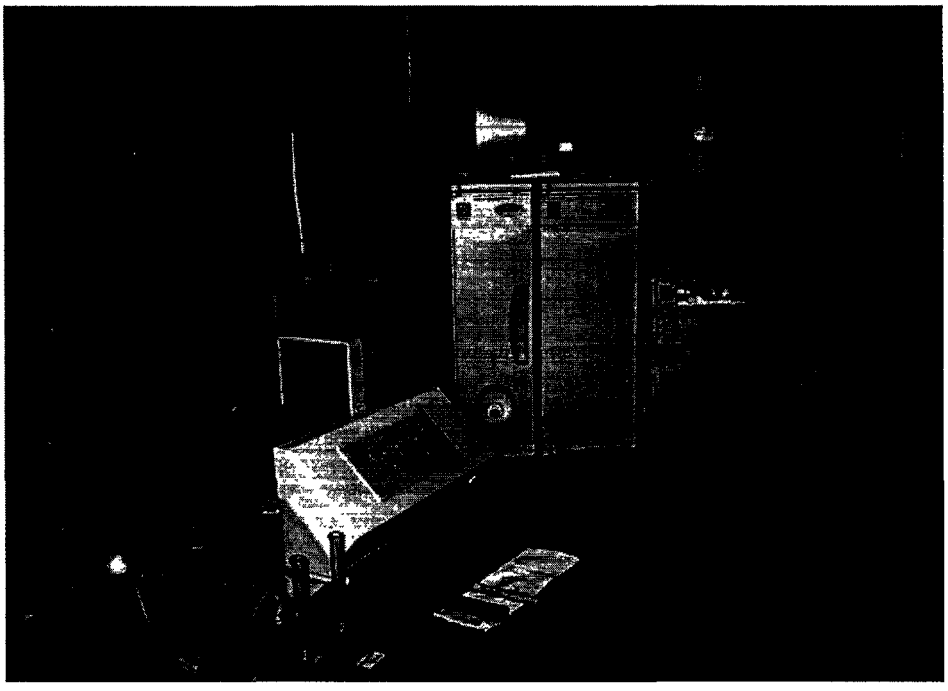


Figure 2-10
On-Site Ion Chromatograph

All anions other than perchlorate (chloride, chlorate, chlorite, nitrate, nitrite, and sulfate) are analyzed on the same system using an AS-17 column, a 10-μg/L loop, and an EG-40 eluent generator configured for gradient analysis. Complete resolution of all of these anions of interest can be evaluated in a single run using the EG-40 to produce a hydroxide eluent gradient based on EPA Method 300.1 modified for use with a hydroxide-selective column (Jackson *et al.* 2000).

At bench-scale, perchlorate is measured using a Dionex 4000i IC with conductivity detection and an AS-16 column, a 500-μL loop, and an autosampler. Based on repeated injections of a 10-μg/L standard, the MDL was 2 μg/L. An AS-11 column is used to analyze for nitrate, nitrite, chlorate, chlorite, chloride and acetate. Also the AS-11 column can be used to determine perchlorate in some experiments with high perchlorate concentrations. Most other anions are measured following Standard Methods (1998) or USEPA methods. Analyses following Standard Methods included ClO_4^-, Cl^-, NO_3^-, NO_2^-.

Analyses following USEPA methods included ClO_3^- and ClO_2^-. The proposed method for ClO_4^- is a modification of USEPA Method 300.1.

It may be noted that the perchlorate analytical detection limits of the pilot-scale and bench-scale systems are not identical. This is primarily a result of the different instrumentation (injection loop) utilized. Even if similar systems were utilized, however, it is anticipated that slight differences will still be reported. These differences would be the result of individual instrument signal (noise) variability, sample handling, and analyst interpretation of instrument response (how to integrate a peak). To ensure the accurate reporting and interpretation of results, a detailed project specific quality assurance program has be developed (see project QAPP – August 16, 2001).

2.3.2 Hydrogen Analysis

There are no standard methods for analyzing hydrogen. Consequently, dissolved H_2 at the pilot-scale system has been analyzed directly using an Orbisphere Model 3654 Portable Micro Logger configured for dissolved hydrogen, as shown in Figure 2-11. Direct measurement of dissolved hydrogen concentrations in the bulk liquid are made utilizing membrane-covered dynamic thermal conductivity (MDTC) sensor technology. The MDTC works by allowing hydrogen gas to permeate through a hydrogen selective membrane and measuring the increase in thermal conductivity against a reference gas, nitrogen.

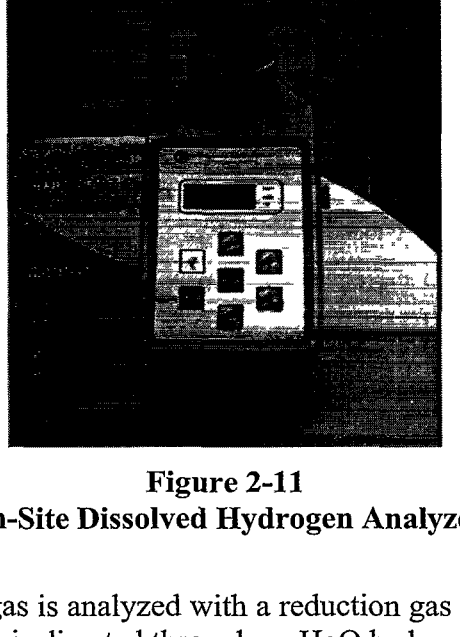


Figure 2-11
On-Site Dissolved Hydrogen Analyzer

At bench-scale, hydrogen gas is analyzed with a reduction gas analyzer (Trace Analytical RGA3). In this method, H_2 is directed through an HgO bed and produces Hg(g), which is

measured by an ultraviolet photometer. For the dissolved-phase H_2 measurement, a headspace analysis is used. One milliliter of liquid sample is transferred from the reactor to a 160-ml serum vial previously outgassed with nitrogen. The vial is then shaken vigorously to liberate the dissolved H_2. Next, a gas-tight syringe is used to sample the headspace (1 ml) and is tested for H_2. Once the H_2 concentration is known, Henry's law and mass balance can be used to determine the dissolved H_2 concentration.

Chapter 3 – Status Report

Since the last progress report (October 2002), research efforts have been focused on the design and implementation of new and modified MBfRs operated as a single reactor. An additional wealth of knowledge has been obtained about the operation, maintenance, design, and start-up of a hydrogen-fed membrane bioreactor system. The engineering analysis of the MBfR process has been initiated to characterize all costs associated with full-scale implementation and operation of an MBfR system. In addition, the project team has submitted documentation to the respective health departments of several states, including California, Utah, Texas, and Massachusetts, to ascertain those issues that need to be addressed before regulatory approval of the process for potable water production could be granted

3.1 MODIFIED MBFR DESIGNS

Three different MBfR designs were evaluated during the last testing period. Operation of the new and modified MBfRs as single reactor systems was based on the knowledge gained through the previous operation of the two-reactors-in-series system.

The following sections document the performance of each single reactor system tested and include:

- Membrana Liqui-Cel
- Modified Mitsubishi (Looped Fiber Design)
- Original Design Mitsubishi (Increased Packing Density – 6%)

3.1.1 Membrana Liqui-Cel

Membrana's Liqui-Cel reactor contains polypropylene hollow fibers separated using a knitted array that is tightly wound around a distribution and collection tube separated by a

central baffle, as shown in Figure 3-1. In Figure 3-2, the knitted array ensures that the all fibers are held an equal distance apart from each other (~ 100 μm). In contrast to the composite hollow fiber membranes, the membrane used by Membrana has only a single microporous layer. The single layer hollow fiber functions identically to the multilayer composite fibers previously used in Mitsubishi modules. The main physical difference between both types of membranes is that the composite fibers are capable of holding higher gas pressures without bubbling. For conventional applications of these hollow fibers membranes (aerating or de-aerating), this is an important feature as the higher gas mass transfer is possible with composite fibers while maintaining the integrity of the membrane fiber and extending the bubble point of the membrane. However, for the MBfR application, this feature (composite vs. single layer microporous) is irrelevant as

the hydraulic and gas pressures are constantly controlled and maintained equal to each other. In addition to reducing system pressures and general stress on the equipment, the lower pressures would help to prevent the inadvertent bubbling of hydrogen and avoid developing a safety hazard (i.e. potentially explosive environment).

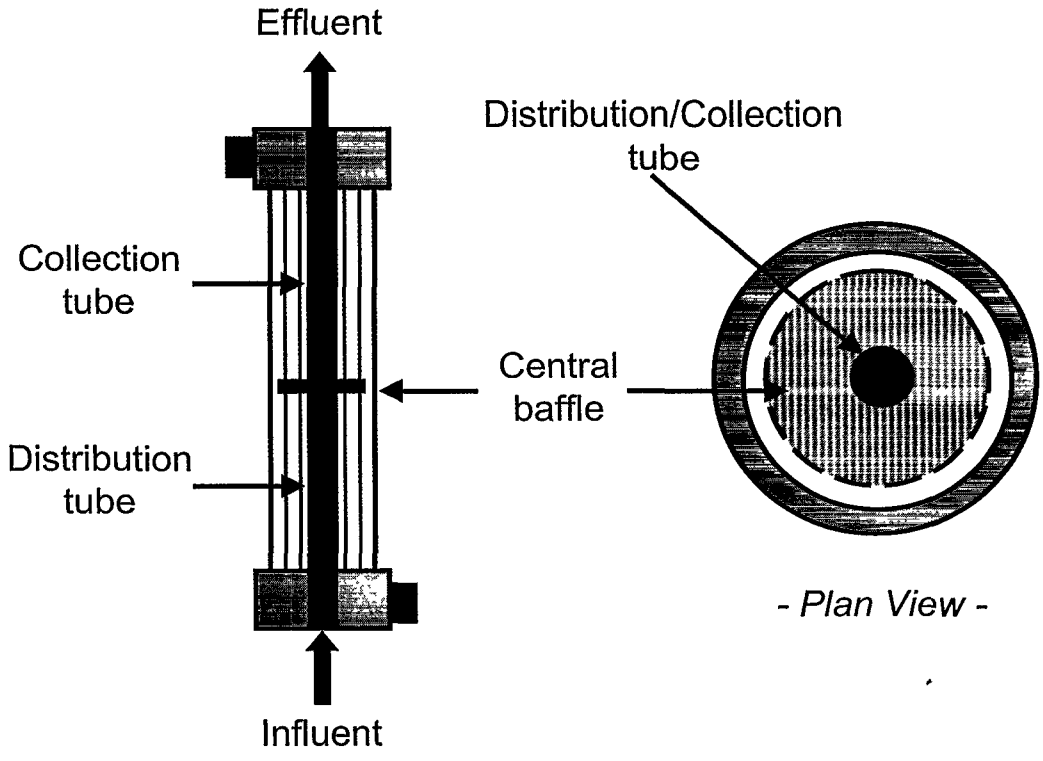


Figure 3-1
Membrana Liqui-Cel Module

Figure 3-2
Membrana Hollow Fiber Knitted Array

As shown in Figure 3-1, liquid enters the reactor and travels through a perforated distribution tube, designed to improve flow distribution by forcing the water past all of the hollow fibers. A central baffle located midway through reactor, directs the liquid around to the second half of the reactor at which point, the liquid must again travel through the fiber bundle and enter the collection tube, perforated similarly to the distribution tube. These unique features (perforated distribution and collection tube, center baffle) ensure that the water comes into contact with all of the fibers regardless of the flowrate.

The intended use of the reactor is for gassing/degassing applications. Consequently, the reactor has a very large membrane surface area, compact design and the ability to handle a high throughput. No modification of the Membrana Liqui-Cel design was performed for its use as an MBfR. As an MBfR, however, hydrogen gas is fed to the upper and lower ends of the reactor to diffuse through the lumens to the biofilm growing on the outside of the fibers. The following Table 3-1 summarizes the specific pilot-scale module and characteristics.

Table 3-1
Membrana Design and Operational Parameters

Parameter	Value
Process	
Membrane Surface Area	45 m^2
Bioreactor Module	
Length	50 cm
Diameter	15.2 cm
Volume	6.9 L
Membrane Fiber	
Outside Diameter	300 µm
Active Length	50 cm
Cross Sectional Area	0.00071 cm^2
Number/module	62691
Packing Density	27.3 percent

3.1.1.1 System Performance

The Liqui-Cel reactor was operated with an HRT of 30 minutes and a recycle flow of 2.2 L/min (Recycle Ratio = 10, linear velocity = 17 cm/min). The reactor was seeded with biomass developed from previous operation of the original Mitsubishi MBfR (3%) and was found to reach steady-sate operation within one week.

For the first three weeks of operation (Figure 3-3), influent DO and nitrate levels were reduced to below detection limits. Perchlorate reduction, however, was limited to approximately 20 percent reduction. During the second week of operation, recycle flow was terminated due to excessive headloss experienced through the reactor, as high as 50 psi. It was impractical to operate the system long-term under such a high pressure, as the

system was not designed for it. Additionally, the hydrogen pressure had to be kept at the low effluent pressure to ensure that the bubble-point was not exceeded at any point along the length of the module. Once the recycle flow was eliminated, interestingly, no change in the steady-state reduction of DO, nitrate, and perchlorate was observed. At this time, it appeared that the improved reactor hydraulics and mass transfer from the module design was able to offset the previous requirement of a moderate to high recycle flow.

As perchlorate reduction rates continued to struggle, two major limitations of the Liqui-Cel design were encountered during regular air scour cleaning. First, the reactor has an extremely high packing density (27.3 percent) and fibers are potted in a tight spiral wound arrangement within the housing. Membrana's intended use of this reactor is for aeration and de-aeration purposes with a clean water. Typically, growth of bacteria is discouraged and strict cleaning protocols are required when used for aeration applications. In contrast, for operation of the MBfR, biofilm growth is promoted and as a result, reactor cleaning is critical for successful operation. The dense knitted fiber array that promotes uniform hydraulics through the fiber bundle, minimizes movement of the fibers dramatically reducing the ability of an air-scour to slough off extra biomass. Secondly, the tight fiber mesh and lack of a drain port near the center baffle prohibited the effective removal of any biofilm that was displaced from the fibers during air scour. Lastly, as the air for the air scour was introduced through the perforated distribution tube, the air did not flow evenly throughout the fiber mass further reducing its effectiveness.

The impact of ineffective cleaning became readily apparent during the fourth week of operation. During this period, the reactor performance significantly suffered as DO and nitrate were no longer being reduced. The breakthrough of DO and nitrate (Figure 3-3) indicated that system hydraulics was being impaired by the buildup of solids and serious short-circuiting was occurring. After continuous air scouring and even mild acid cleaning, system performance was unable to be restored and Liqui-Cel reactor was taken offline.

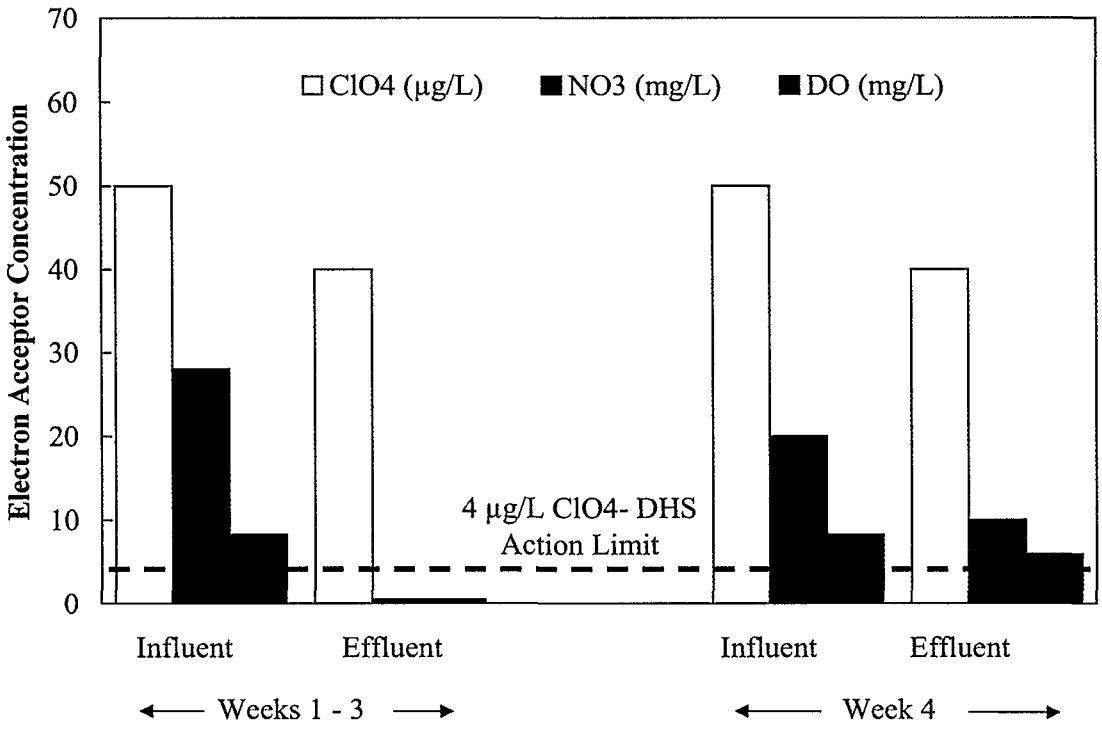


Figure 3-3
Summary of Liqui-Cel Performance

3.1.1.2 Liqui-Cel Module Investigation

As a means to understand the cause of the Liqui-Cel's failure, a thorough investigation of the internals of the reactor design was performed by dissecting the module. A small longitudinal slice of the reactor housing was removed to evaluate the initial status of the membranes. Interestingly, seen in Figure 3-4, there was a large visual difference between the two halves of the membrane cartridge. The lower half of the membrane cartridge (influent side) up to the baffle was fairly clean and free of biomass. However, the upper half of the membrane cartridge (effluent side) was covered with obvious biomass growth. This observation can be more closely seen in Figure 3-5.

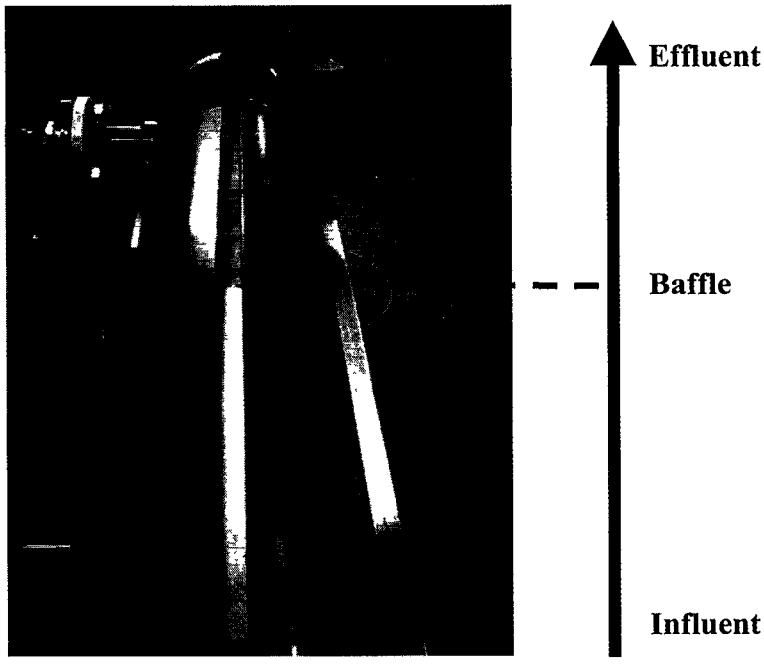


Figure 3-4
Liqui-Cel Membrane Fibers Revealed

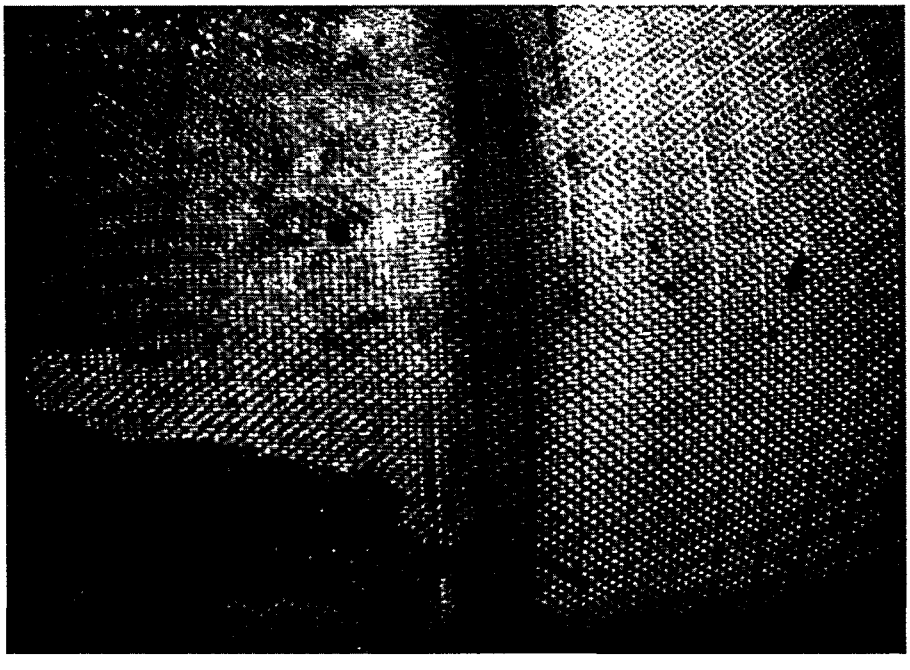


Figure 3-5
Closeup of Upper and Lower Halves
of the Membrane Cartridge with Center Baffle

These observations of the outer fiber areas led us to hypothesize that the membrane fouling by biomass overgrowth was occurring primarily in areas in which the water initially enters the membrane fiber mesh. As evident above for the upper half of the module, the biomass would accumulate on the outer portion of the fiber bundle. Conversely, the majority of growth would accumulate next to the perforations in the distribution tube on the lower half of the module, where the raw water enters the fiber bundle through the distribution tube.

An interesting observation given additional longitudinal cross sectional views (Figure 3-6 and Figure 3-7) is how densely packed the fibers are within the module. This further illustrates how difficult it would be to remove any biomass that would build-up within the fiber bundle.

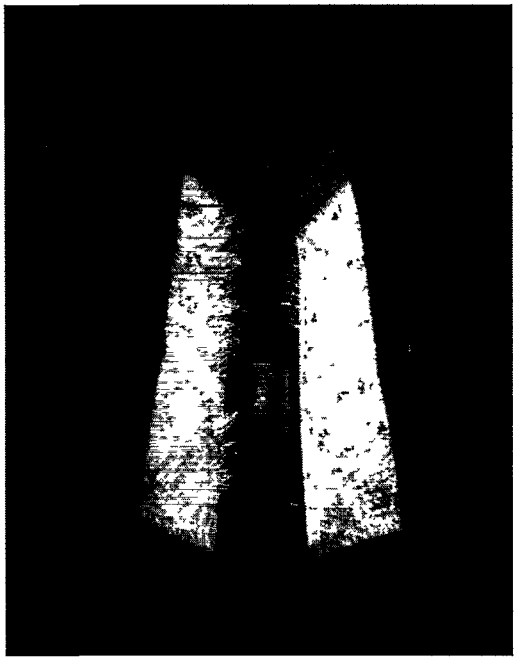


Figure 3-6
View of Center Baffle and Insides of the Perforated Distribution and Collection Tubes

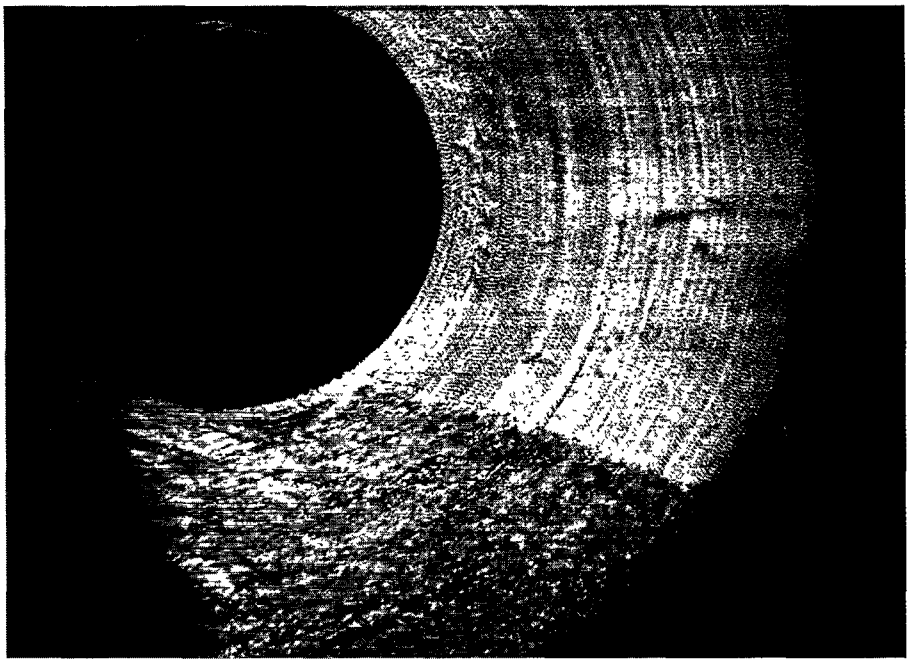


Figure 3-7
Cross-Sectional View of Membrane Cartridge in Housing

3.1.1.3 Liqui-Cel Conclusions

The Liqui-Cel design is originally intended for applications involving the gassing/degassing of water. The main focus of testing this design was to compare performance and design features to that of the MBfR modules previously tested. The following is a summary of key design elements of the Liqui-Cel design.

- Single layer microporous hollow fibers
- Polypropylene fibers with hydrophobic characteristics
- Patented and flow distribution system with the module to improved hydraulics
- High membrane surface area

All of these features are highly desired and optimal for gassing/degassing applications. However, some aspects of these design features were found to be detrimental to the operation and performance of the module for its application as a MBfR. Based on the evaluation of the Liqui-Cel design operated as an MBfR, the project team was able to identify additional key features, outlined below, that would be required for successful operation and design of an optimized MBfR module.

Reactor Cleaning / Solid Removal. The importance of reactor cleaning was documented during operation of the first generation MBfR systems (Progress Report 3). Air scour cleaning was found to be an effective way to remove biomass overgrowth, control short-circuiting of flow within the reactor, prevent calcification buildup on the fibers, and

control sulfate reducing bacteria. Regular air scour cleaning was implemented during operation of the Liqui-Cel design. However, the reactor was limited in its ability to effectively remove solids from the system. As air scour cleaning was virtually ineffective, solids accumulated within the reactor resulting in increasing headloss through the reactor and serious short-circuiting. These quickly led to a reduction and ultimately a failure of the system's ability to remove dissolved oxygen, nitrate and perchlorate. Given the experience and knowledge gained operating the Liqui-Cel design, all future modification in the design of an effective MBfR module must include a means for solids to be removed from the system.

Membrane Fiber Packing Density / Surface Area. The Liqui-Cel reactor contains more than 60,000 hollow fiber membranes resulting in a fiber packing density of 27 percent and a total membrane surface area of 42 m^2. The original Mitsubishi reactors contained only 8000 fibers (membrane surface area = 7.7 m^2) had a packing density of only 3 percent. Failed operation of the Liqui-Cel reactor was attributed to the extremely high packing density and inability for fibers to freely move during air scouring. Although, a high surface area may allow for more reduction to take place and reduce or eliminate the need for recirculation, it was obvious that a 27 percent packing density was too high. Additional testing must be done to evaluate the optimal membrane packing density, while maximizing membrane surface area and ensuring that effective cleaning of the fibers if possible with regular air scour.

Membrane Fiber Material / Composition. Evaluting different types of hollow membrane fibers from different manufacturers was of interest to the project team. In previous testing periods, only Mitsubishi Rayon's composite hollow fiber membranes were tested. Mitsubishi's composite fibers, composed of nonporous polyurethane layer sandwiched between two microporous polyethylene layers, were designed to withstand higher gas pressures and to reduce the potential for bubbling of hydrogen through the microporous layer controlled by the middle layer. The Liqui-Cel reactor uses Membrana's polypropylene single-layer microporous membranes. For operation in a gassing/degassing application, this feature is important because the shellside (water) and lumenside (gas) pressures may not always be in balance with each other. However, from an operational and safety perspective when using hydrogen gas, it is recommended that both shellside and lumenside pressures be equal when the fibers are used in a MBfR application. Given this operational recommendation, composite membranes have no significant advantage over a single layered membrane during typical operation and nearly any hydrophobic microporous or composite membrane can be used. Should a failure in the system occur, however, membranes with a higher bubble point, may be considered safer.

3.1.2 Modified Mitsubishi (Looped-Fiber Design)

Modifications of the original Mitsubishi MBfR design were performed by Mitsubishi Rayon Corporation (Japan) and shipped to the project team for evaluation. Figure 3-8 presents a conceptual diagram of this modified module, which incorporates several

different design features to improve performance. The following details key feature of the new Mitsubishi design and Table 3-1 summarizes the specific module and membrane parameters used for pilot-scale testing.

Hydraulics. The modified design includes three new features to the MBfR module designed to improve hydraulic performance. To address the project teams' concern about short-circuiting with the MF/UF designed reactor having influent and effluent ports on the same side of the reactor, the manner in which water enters the reactor was modified. Included in this design is a ¾ inch I.D. influent port with a small ¾ inch center inlet located in the center of the reactor. The center inlet oriented so that water enters the reactor and is directed downwards toward the fiber potting. Mitsubishi's reasoning is that the entry of water is this manner would create a more even flow distribution as it moves up the reactor in tandem with the second feature. Approximately a third of the way downstream from the influent port, Mitsubishi also positioned a central baffle ring. Approximately one inch in thickness, the central baffle ring is designed to redirect the flow along the sides of the reactor through the fiber bundle. Finally, the outlet port has been modified such that water exits the reactor through center of the end cap. This outlet feature was made possible by an alternative membrane fiber arrangement and potting.

Membrane Fiber Potting. The same composite hollow fiber membranes are used in this new module. However, instead of fibers potted at both end of the reactor, they are looped in half with both ends of the fiber potted at the influent end of the module. The looped "end", technically the middle of the fiber length, is free to move about at the effluent end of the module. This looped fiber – free end design is advantageous because the fiber movement is not restricted as they are when potted at both ends. Having nearly a full range of motion allows air scour cleaning to more effectively jostle fibers to remove biomass solids that accumulate. In addition, it makes it possible for water to exit the reactor from the center of the endcap rather than the side of the reactor. The drawback from this design is that there is no quick way to evacuate any condensation that may collect in the fibers, thereby decreasing hydrogen transfer.

Membrane Surface Area. Mitsubishi also increased the packing density from 3 to 20 percent (approximately 40 percent within the central baffle ring). Now with 50,000 fibers in nearly the same module housing, the membrane surface area was increased by more than 6 times from 7.7 m^2 (original 3 percent MBfR) to 48.4 m^2. This dramatic increase in membrane surface area is designed to ensure complete reduction of all electron acceptor species occurs within in a single reactor configuration rather than two reactors in series. Mitsubishi also intended the increase in membrane surface area to allow for a higher loading of electron acceptors as well, which would increase system throughput.

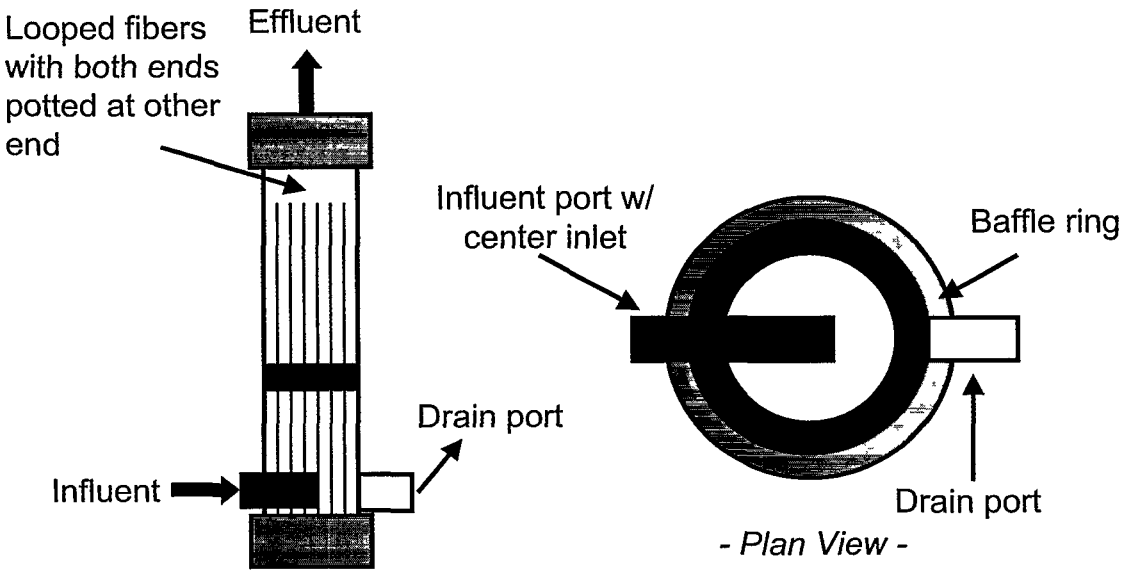


Figure 3-8
Modified Mitsubishi (Looped-Fiber Design) Module

Table 3-2
Modified Mitsubishi (Looped-Fiber Design) Design and Operational Parameters

Parameter	Value
Process	
Membrane Surface Area	48.4 m^2
Bioreactor Module	
Length	110 cm
Diameter	14 cm
Volume	13.5 L
Membrane Fiber	
Outside Diameter	280 µm
Active Length	110 cm
Cross Sectional Area	0.00062 cm^2
Number/module	50000
Packing Density	20 percent

3.1.2.1 Modified Mitsubishi System Performance

The modified Mitsubishi reactor was operated with HRTs between 10 and 30 minutes and recycle flows corresponding to linear velocities of 17 to 154 cm/min. The reactor was seeded with biomass developed from previous operation of the original Mitsubishi MBfR (3 percent) and was found to reach steady-sate operation within one week. Throughout the course of testing, different operating conditions were applied to the system and the system performance was evaluated with respect to:

- Hydraulic Retention Time
- Recycle Flow Rate / Linear Velocity
- Effectiveness of Air Scouring Cleaning

3.1.2.1.1 Hydraulic Retention Time

The modified Mitsubishi module was initially operated with an HRT of 30 minutes and reached steady state within one week. Complete removal of both nitrate and DO was observed, and 70 percent reduction of perchlorate was also observed.

Following operation of the modified Mitsubishi at an HRT of 30 minutes, the system flowrate was increased to evaluate performance at several different HRTs. As seen in Figure 3-9, complete reduction of DO was easily attained at even the shortest HRTs. Complete denitrification was maintained as long as the theoretical hydraulic retention time was greater than 15 minutes. At lower HRTs (less than 15 minutes) nitrate breakthrough was occurring. The average maximum perchlorate reduction observed to date has been 70 percent corresponding to HRTs of greater than 24 minutes. Influent perchlorate concentrations average 50 µg/L corresponding to an effluent concentration of 10 µg/L.

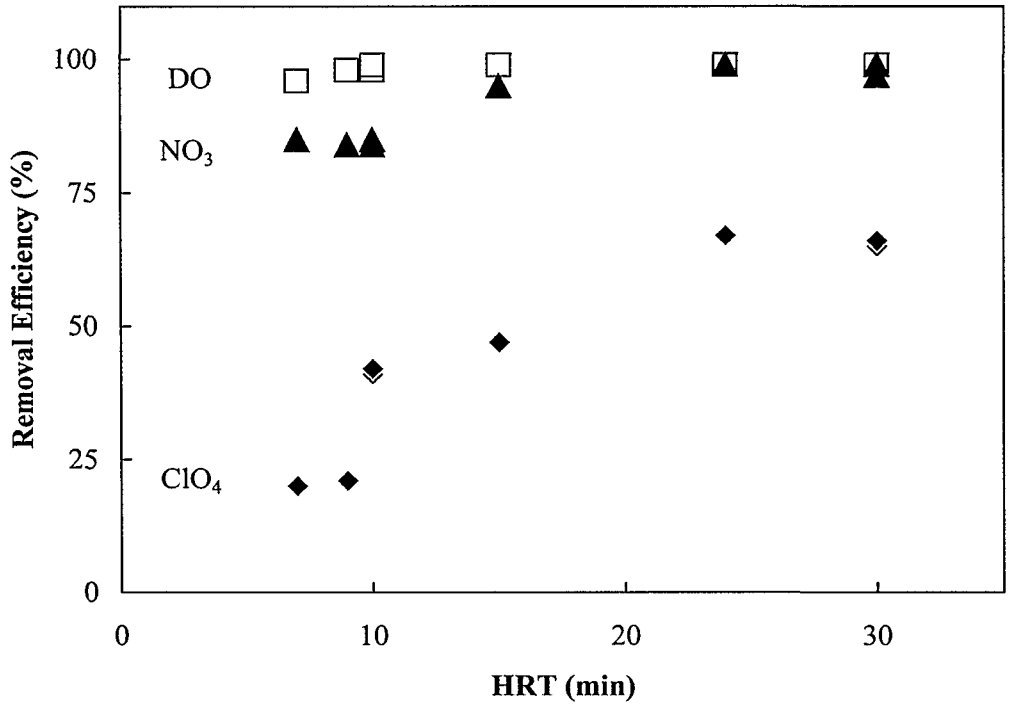


Figure 3-9
Modified MBfR Performance (Removal Efficiency)

Figure 3-10 similarly summarizes reactor performance with respect to apparent substrate flux. The apparent perchlorate flux suffers dramatically when the HRT is less than 10 minutes and can be further explained by referring back to Figure 3-9. Interestingly, nitrate breakthrough first occurs at an HRT of 10 minutes, which indicates that more nitrate is entering the system than the biofilm can utilize. With excess nitrate present, it appears that some of the bacteria previously degrading perchlorate stopped that function either as a result of inhibition or as a result of switching their metabolic function from perchlorate to nitrate reduction. Since all of the perchlorate reducing organisms identified to date can also reduce nitrate, it is not surprising that a dramatic decrease in perchlorate reduction is associated with the breakthrough of nitrate.

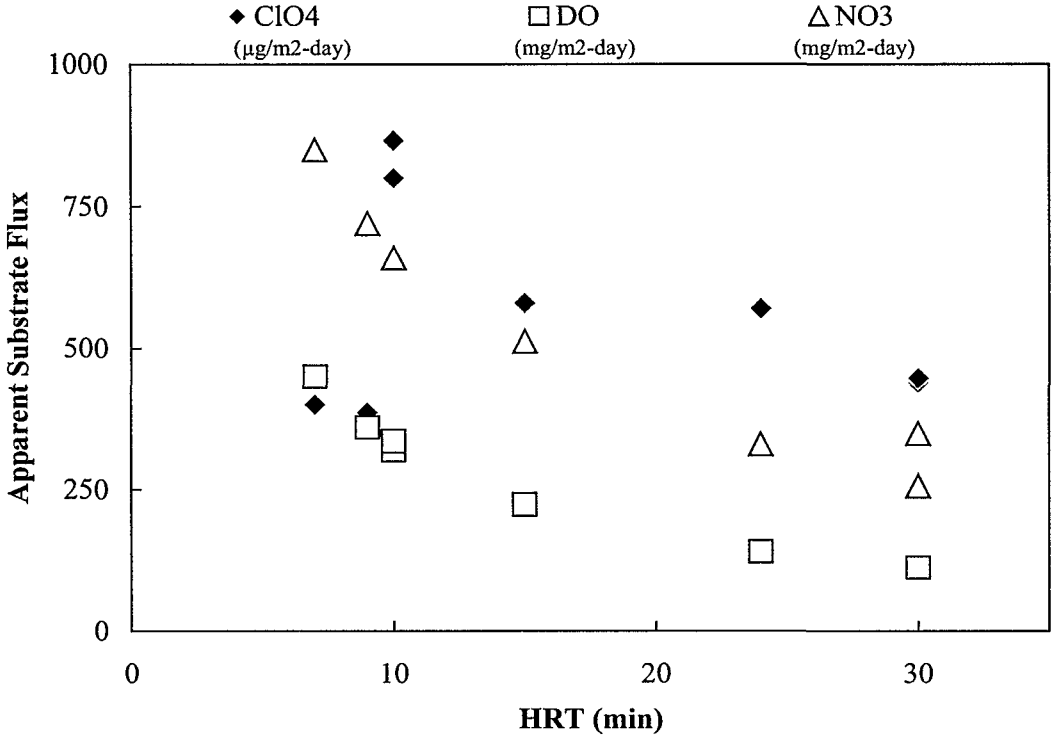


Figure 3-10
Modified MBfR Performance (Apparent Substrate Flux)

Testing with the modified Mitsubishi is still ongoing to find a means to achieve perchlorate reduction below 4 µg/L. Operation of the system to date clearly demonstrates that when the modified Mitsubishi is operated below an HRT of 10 minutes, performance dramatically suffers. Remaining testing of the modified Mitsubishi will focus operating at HRTs between 15 and 30 minutes.

3.1.2.1.2 Effect of Recycle

One of the goals of the Mitsubishi reactor modification is to address the hydraulic limitation of the original design. In addition to testing the modified reactor with varying HRTs, the recycle flow also altered resulting in linear velocity ranging from as low as 61 to 154 cm/min. The average linear velocity observed within the MBfR during all testing was 120 cm/min.

In the original MBfR design, it was shown that reactor performance improved with increased recycle flow. Changes in recycle flow affect both the linear velocity and overall hydraulics through the module, which can improve mass transfer to the biofilm. The hydraulic shortcomings of the original design appear to be improved with the modified design. Summarized in Figure 3-11, the system was operated at two different HRTs each at two different recycle flow rates corresponding to linear velocities of 61 and 154 cm/min. It is important to note that each condition represents steady-state operation as the system was operated and monitored for a minimum of one week.

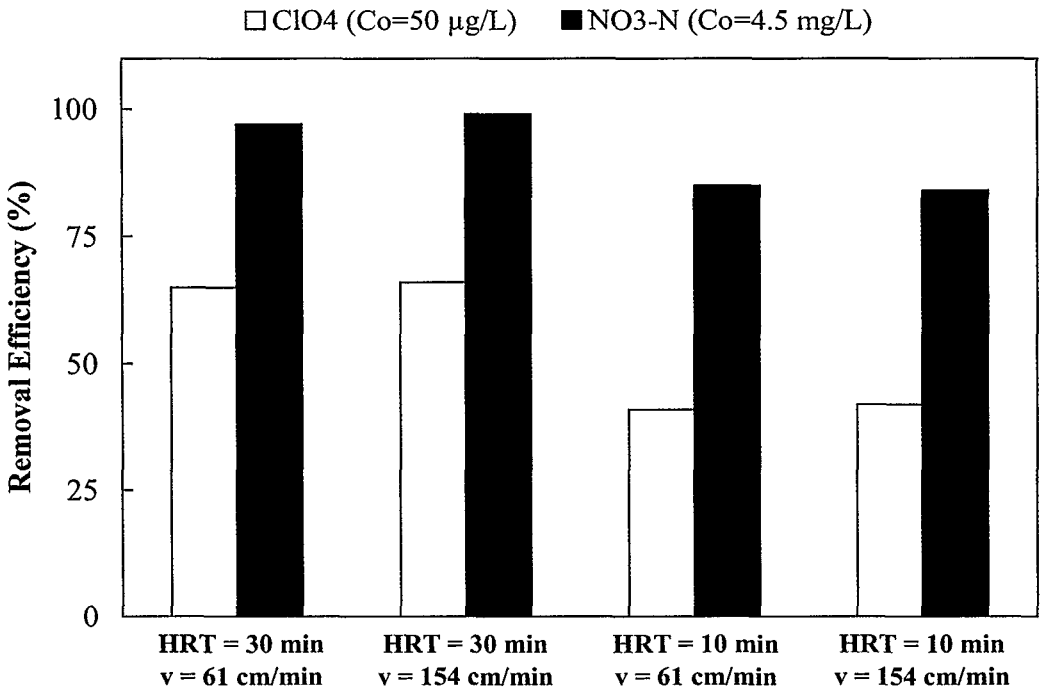


Figure 3-11
Effect of Recycle on Modified Mitsubishi

It can be clearly seen in Figure 3-11 that system performance did not improve when high recycle flow rates were applied when operated at the same HRT. These results indicate that the modified Mitsubishi can be operated with a lower and more reasonable recycle flowrates while maintaining system performance. This promising data also points

favorable toward the economic feasibility of full-scale application of the MBfR. With the original MBfRs, an enormously high recycle was utilized to achieve sufficient removal rates. Full-scale operation at and extremely high recycle flow rates would be costly and operationally difficult if large recycle pumps were to be required.

3.1.2.1.3 Air Scour Modification

Reactor cleaning is critical to successful operation of the MBfR and is an important issue for operation of the modified Mitsubishi reactor considering it contains 50,000 fibers (20 percent packing density). The improvements to the design (baffle ring and influent ports) are great for hydraulics but were found to be poor for effective air scour cleaning and solids removal with the high fiber packing density.

The modified Mitsubishi module does contain a side drain port. However, the location is not ideal because it is located below the baffle. As fibers are concentrated within the baffle ring, the fiber packing density is increased from 20 to 40 percent. This makes the removal of solids above the baffle ring operationally difficult.

The advantage of having looped fibers potted at one end allowed for freedom of movement of the fibers during operation and air scour. With the baffle ring located in the lower half of the module, effective movement of the fibers during air scour was limited above the baffle ring. Below the baffled ring, the fibers could not be effectively clean, as seen in Figure 3-12. As solids accumulated on the fibers and on the walls of the housing below the baffle ring, hydraulics were impaired, cleaning efficiency was poor, and sulfate reduction was occurring.

As a means to improve the method of air scour, the reactor was further modified by the project team by adding six air scour ports on the sides of the reactor housing as illustrated in Figure 3-13. After adding the additional ports, air scour cleaning was improved and the biomass buildup below the baffle ring was minimized. In addition, air scour cleaning directly above the baffle ring was improved because an even distribution of air scour bubbles was allowed to travel up through the fibers.

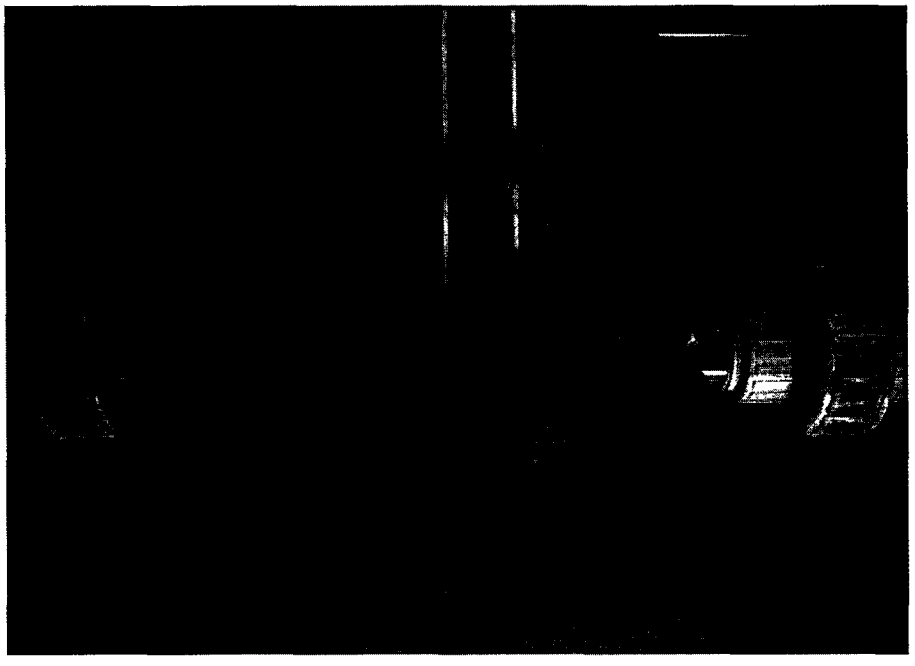


Figure 3-12
Biomass Buildup Before Modified Air Scour

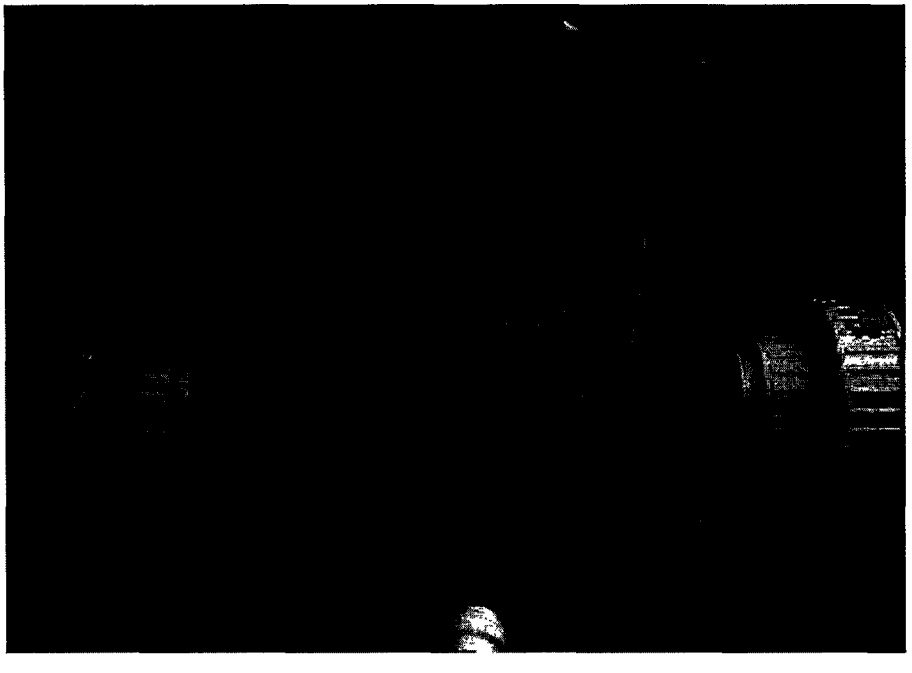


Figure 3-13
Effect of Air Scour Modification Improvement

3.1.2.2 Modified Mitsubishi Conclusions

Mitsubishi Rayon, Corp. manufactured a modified version of the first generation MBfR by adding distinct features to address hydraulic limitations. The main focus of testing this design was to compare performance and design features to that of other MBfR modules previously tested. The following is a summary of key design elements of the modified Mitsubishi design.

- Looped fibers potted at a single end
- Baffle Ring for improved hydraulics
- Additional air scour ports added by the project team
- High membrane surface area

Membrane Fibers. Membrane fibers in the modified design are potted at one end of the reactor. This feature improved the fiber's freedom of movement and was designed to allow for a more effective air scour cleaning. The increased membrane surface area as compared to the original design resulted in similar reduction of DO, nitrate, and perchlorate to what was only previously achieved with the two-reactor-in-series MBfR system.

Perchlorate reduction rates, however, have been limited to 70 percent. Efforts are currently focussed on operating the modified reactor to achieve reduction of perchlorate to below the 4 µg/L CaDHS action limit.

Baffle Ring. The baffle ring was intended to improve system hydraulics by limiting short-circuiting along the sides of the reactor and forcing water through the center of the fiber bundle. Although an improvement in the mass transfer, as lower recycle flows were sufficient to maintain steady-state reduction, the O&M associated with the location of the baffle posed some problems. Cleaning efficiency is poor as the packing density through the baffle ring is too high to allow sloughed biomass to pass. Some minor reengineering may be sufficient to remedy this problem.

Air Scour Modification. The need for an improved air scouring was identified for this reactor design and was modified by the project team. The addition of several air scour ports was successful and would be recommended for future designs. Not only does the inlet water need to be supplied to the module in an even distribution, but air scour must be supplied with the same principles in mind. The air scour bubbles tend to travel up the side of the reactor along the inside walls. Consequently, at least two strategically positioned air scour ports are recommended for even cleaning.

3.1.3 Original Design Mitsubishi (Increased Packing Density - 6%) Modified

Evaluation of the two alternative MBfR designs (Liqui-Cel and Modified Mitsubishi) highlighted points regarding membrane fiber packing density and air scour cleaning methods. Based on the understanding of the original design and the two alternative designs, a modified version of the original design was created and tested. Figure 3-14 presents a conceptual diagram of this modified module, which incorporates several different design features to improve performance.

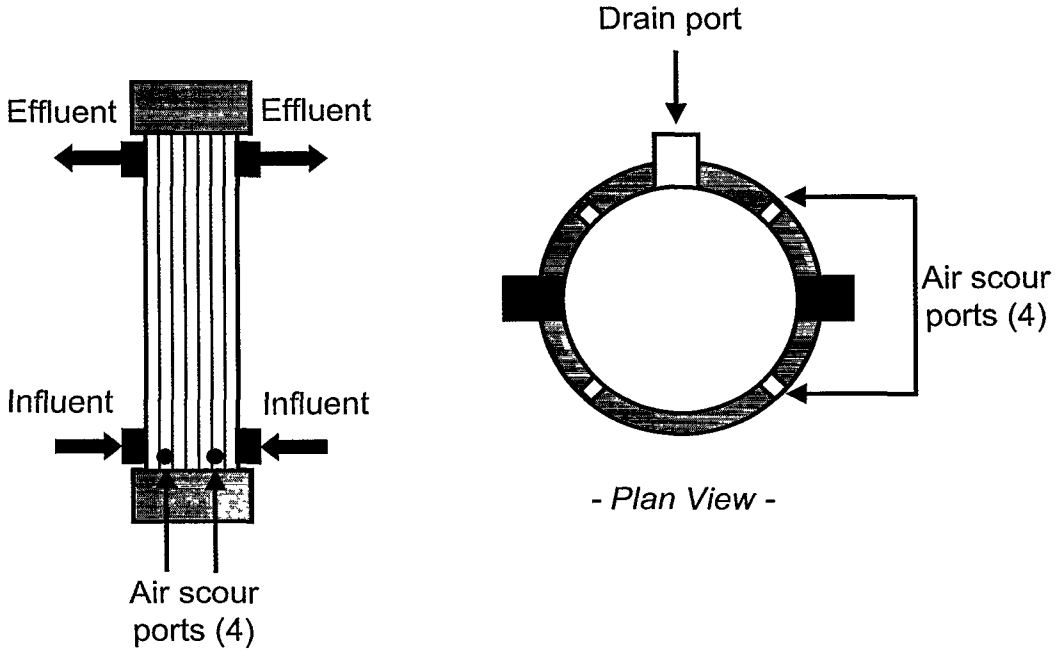


Figure 3-14
Original Design Mitsubishi (Increased Packing Density – 6 Percent) Modified Module

Membrane Fiber Packing Density. It was apparent from the testing of the Liqui-Cel and Mitsubishi Loop-Fiber Design reactors that 27 percent packing density was too high for successful application as an MBfR and 20 percent may be too high if extreme steps for fouling control by proper air scour are not incorporated. The Original Mitsubishi design contained only a 3 percent packing density. For this new system, we are evaluating a 6 percent packing.

Module Modifications. The first modification of the original design includes adding two influent and effluent ports so that water would more even be distributed in the reactor and reduce the potential of short circuiting. By adding additional influent and effluent ports, the existing original influent port could then be used as a drain port for solids removal. The second modification involved the addition of an improved air scouring system. Four

air scour ports, independent of the influent ports were added 90 degrees apart from each other to promote efficient and evenly distributed air scour.

Testing of this modified 6 percent reactor has been initiated and Table 3-3 summarizes the specific module and membrane parameters used for pilot-scale testing.

Table 3-3
Mitsubishi (6 Percent) Design and Operational Parameters

Parameter	Value
Process	
Membrane Surface Area	14.5 m^2
Bioreactor Module	
Length	110 cm
Diameter	14 cm
Volume	13.5 L
Membrane Fiber	
Outside Diameter	280 µm
Active Length	110 cm
Cross Sectional Area	0.00065 cm^2
Number/module	15000
Packing Density	6 percent

3.2 ENGINEERING ANALYSIS

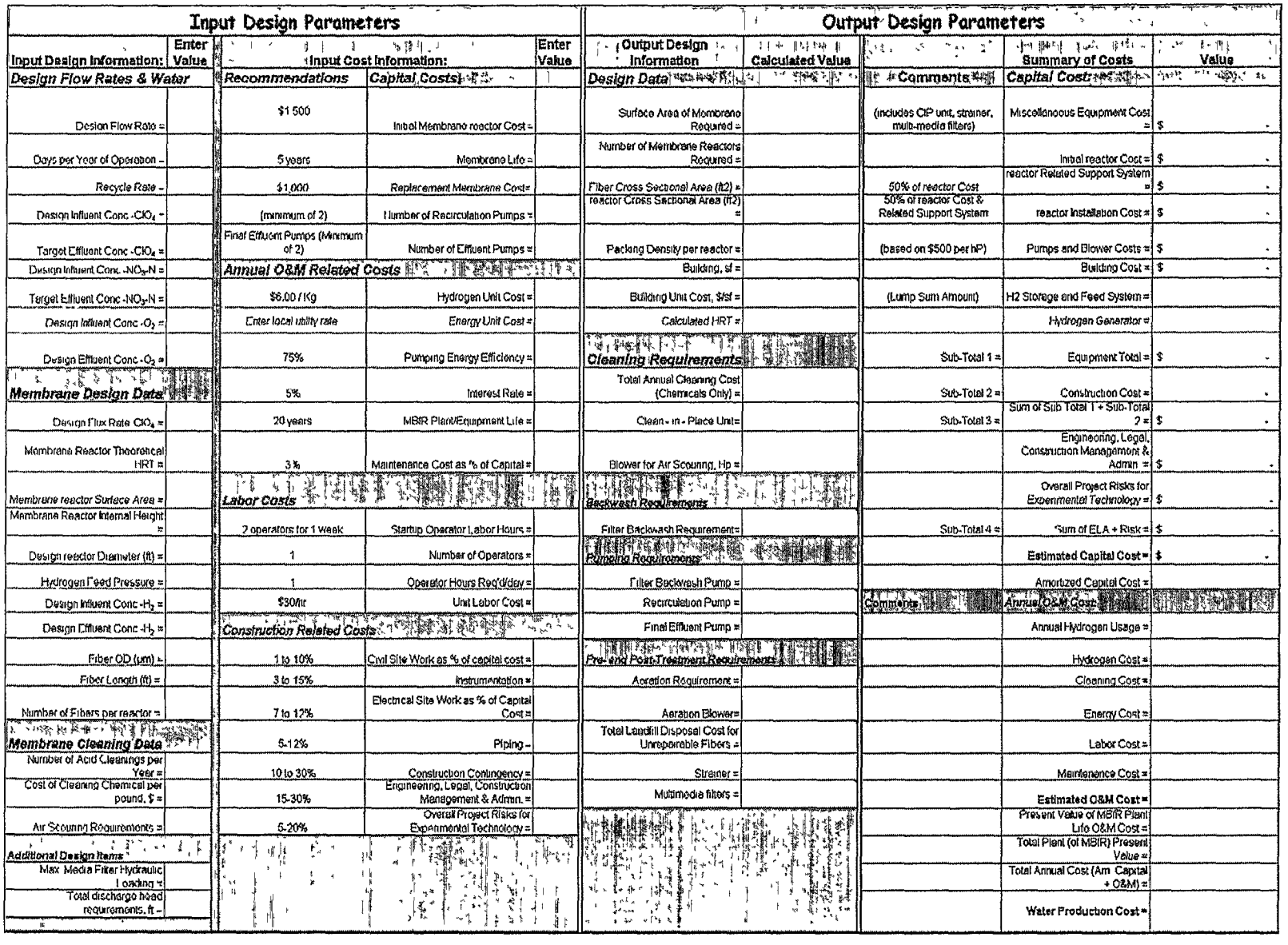
This chapter is dedicated to providing general information regarding the cost model and outlines the development of the model for future economic analysis. The complete analysis will be presented in the Draft Final Report, and will be based on the operation and performance of the optimal pilot-scale bioreactor system.

3.2.1 Cost Estimating

There are four levels of cost estimating: order-of-magnitude, conceptual, preliminary, and definitive. As their names imply, each cost estimate increases in detail and is applied to various phases of the design process.

A conceptual cost estimate may be applied to an existing structure or treatment plant, or it may be applied to a new facility were site specific information is not yet available. Therefore, this type of estimate was applied to the MBfR full-scale economic evaluation. Typically a schedule of values from previous projects that are similar in nature can be utilized as a starting point. Because the MBfR process is an innovative technology, similar projects are not currently available for reference. However, historical data is available for the auxiliary equipment, facility structure, and other more common construction related costs.

As shown in Figure 3-15, the model has been designed to allow users to input specific design information and make preliminary cost estimates based on design flow and perchlorate concentrations. The model begins by having the user input influent water quality parameters and design flow rates, and calculates various design parameters and conceptual level cost information. Where applicable (i.e. construction cost estimates) percent ranges have been provided as a guide. These ranges are based on experience with water treatment plant design and will vary with site specific information.



Input Design Parameters						Output Design Parameters				
Input Design Information:	Enter Value	Input Cost Information:		Enter Value	Output Design Information	Calculated Value	Comments	Summary of Costs	Value
Design Flow Rates & Water		**Recommendations**	**Capital Costs**		**Design Data**			**Capital Costs**	
Design Flow Rate =		$1 500	Initial Membrane reactor Cost =		Surface Area of Membrane Required =		(includes CIP unit, strainer, multi-media filters)	Miscellaneous Equipment Cost =	$ -
Days per Year of Operation =		5 years	Membrane Life =		Number of Membrane Reactors Required =			Initial reactor Cost =	$ -
Recycle Rate =		$1,000	Replacement Membrane Cost=		Fiber Cross Sectional Area (ft2) =		50% of reactor Cost	reactor Related Support System =	$ -
Design Influent Conc -ClO_4 =		(minimum of 2)	Number of Recirculation Pumps =		reactor Cross Sectional Area (ft2) =		50% of reactor Cost & Related Support System	reactor Installation Cost =	$ -
Target Effluent Conc -ClO_4 =		Final Effluent Pumps (Minimum of 2)	Number of Effluent Pumps =		Packing Density per reactor =		(based on $500 per hP)	Pumps and Blower Costs =	$ -
Design Influent Conc -NO_3-N =		**Annual O&M Related Costs**			Building, sf =			Building Cost =	$ -
Target Effluent Conc -NO_3-N =		$6.00 / Kg	Hydrogen Unit Cost =		Building Unit Cost, $/sf =		(Lump Sum Amount)	H2 Storage and Feed System =	
Design Influent Conc -O_2 =		Enter local utility rate	Energy Unit Cost =		Calculated HRT =			Hydrogen Generator =	
Design Effluent Conc -O_2 =		75%	Pumping Energy Efficiency =		**Cleaning Requirements**		Sub-Total 1 =	Equipment Total =	$ -
Membrane Design Data		5%	Interest Rate =		Total Annual Cleaning Cost (Chemicals Only) =		Sub-Total 2 =	Construction Cost =	-
Design Flux Rate ClO_4 =		20 years	MBfR Plant/Equipment Life =		Clean - in - Place Unit=		Sub-Total 3 =	Sum of Sub Total 1 + Sub-Total 2 =	$ -
Membrane Reactor Theoretical HRT =		3 %	Maintenance Cost as % of Capital =		Blower for Air Scouring, Hp =			Engineering, Legal, Construction Management & Admin =	$ -
Membrane reactor Surface Area =		**Labor Costs**			**Backwash Requirements**			Overall Project Risks for Experimental Technology =	$ -
Membrane Reactor Internal Height =		2 operators for 1 week	Startup Operator Labor Hours =		Filter Backwash Requirement=		Sub-Total 4 =	Sum of ELA + Risk =	$ -
Design reactor Diameter (ft) =		1	Number of Operators =		**Pumping Requirements**			**Estimated Capital Cost =**	$ -
Hydrogen Feed Pressure =		1	Operator Hours Req'd/day =		Filter Backwash Pump =			Amortized Capital Cost =	
Design Influent Conc -H_2 =		$30/hr	Unit Labor Cost =		Recirculation Pump =		Comments	**Annual O&M Cost**	
Design Effluent Conc -H_2 =		**Construction Related Costs**			Final Effluent Pump =			Annual Hydrogen Usage =	
Fiber OD (um) =		1 to 10%	Civil Site Work as % of capital cost =		**Pre- and Post-Treatment Requirements**			Hydrogen Cost =	
Fiber Length (ft) =		3 to 15%	Instrumentation =		Aeration Requirement =			Cleaning Cost =	
Number of Fibers per reactor =		7 to 12%	Electrical Site Work as % of Capital Cost =		Aeration Blower=			Energy Cost =	
Membrane Cleaning Data		5-12%	Piping =		Total Landfill Disposal Cost for Unreparable Fibers =			Labor Cost =	
Number of Acid Cleanings per Year =		10 to 30%	Construction Contingency =		Strainer =			Maintenance Cost =	
Cost of Cleaning Chemical per pound, $ =		15-30%	Engineering, Legal, Construction Management & Admin. =		Multimedia filters =			**Estimated O&M Cost =**	
Air Scouring Requirements =		5-20%	Overall Project Risks for Experimental Technology =					Present Value of MBfR Plant Life O&M Cost =	
Additional Design Items								Total Plant (of MBfR) Present Value =	
Max Media Filter Hydraulic Loading =								Total Annual Cost (Am Capital + O&M) =	
Total discharge head requirements, ft =								**Water Production Cost =**	

Figure 3-15
Sample Screen from MBfR Cost Model

3.2.2 Input Variables

Site specific data is essential for an engineering analysis. If this data is not available at the time the model is run, estimates may be used based on recommended data provided in the model. The variables for the input section of the cost model include:

- Design Flow Rates
- Water Quality
- Membrane Design Data
- Membrane Cleaning Data
- Capital Costs
- O&M Costs
- Labor Costs, and
- Construction Related Costs

3.2.2.1 Design Flow Rates and Water Quality

The user may enter a specific design flow rate, up to 2500 gpm. Example design flow rates of 500, 1000, and 2500 gallon per minute (gpm) will be run to represent reasonable size full-scale treatment flow rates, or at least provide design flow rates suitable for modular construction.

Along with design flow rate, the users must enter influent water quality conditions. Required parameters include influent perchlorate concentration, target effluent perchlorate concentration, influent and target effluent nitrate concentration, and influent and effluent dissolved oxygen concentration.

3.2.2.2 Membrane Design

The membrane design data is manufacturer and design specific and therefore critical to the input design section of the cost model. Preliminary estimates indicate that the variables within this section may have the single greatest impact on the overall cost of a full scale MBfR plant. Included in this section are:

- Perchlorate flux rate
- Theoretical Hydraulic Retention Time (HRT)
- Dimensions of the membrane module
- Number, length and diameter of membrane fibers

For new systems, perchlorate flux rate will need to be provided by the membrane module manufacturer or from pilot test data. The remaining membrane design data (listed above) should be available from the membrane module manufacturer.

3.2.2.3 Membrane Cleaning

Given the influent water quality data for the existing MBfR pilot plant, daily air scouring and one mild citric acid cleaning per month has been necessary to control biofilm growth to prevent biomass accumulations that limit mass transfer. Included in the cost of membrane cleaning are: number of cleanings per year, cost of citric acid, and air scouring requirements (cfm).

3.2.2.4 Capital Cost

The capital cost section includes equipment, annual O&M, labor costs, and construction related costs. As each of these are major sections, and therefore discussed individually.

Equipment
The equipment associated with a new MBfR plant includes the initial membrane modules, replacement membranes, re-circulation pump(s), aeration, multimedia filters, effluent pump(s), and facility structure. It is assumed for the purpose of the cost model that the membranes will be replaced every 5 years and that all other equipment has a expected life of 20-years. This will vary with capacity, water quality, maintenance, and use. Therefore, it remains an input variable and effects the equipment costs and ultimately the annual O&M costs.

The MBfR process will remove any residual associated oxygen in the treatment process. Therefore, aeration is required prior to entry to the distribution system. However, using an aeration tank to introduce dissolved oxygen into the water supply will cause the system to loose head and an effluent pump(s) will be required to boost the pressure.

Annual O&M Costs
Annual O&M costs are associated with daily consumable variables. These consumables include utilities as well as daily maintenance of equipment. For subsequent cost analysis, the membrane life will be assumed to be 5 years, with all other equipment life at 20 years. The O&M variables included in the cost model are:

- Annual Hydrogen Costs
- Cleaning Costs
- Energy Costs
- Labor Costs
- Maintenance Costs

Labor Costs
The labor costs associated with operating a MBfR plant is estimated to be minimal. This is due to automation of the system. The startup time will require the most operator attention and training to ensure proper installation, operating conditions, and that the biofilm is developing to an effective mass. Frequency of sampling and analysis

requirements will depend upon design flow rate, operating conditions (i.e. optimization period and plant upsets will have a higher sampling frequency).

Construction Related Costs

Construction related costs are those costs associated with construction, and for an experimental technology includes a risk factor. The analysis for the final report will evaluate a range of construction related costs (as a percentage of the capital cost), based on experience with water treatment plant construction. The items include the following items listed in Table 3-4:

Table 3-4
Range of Construction Related Costs

Construction Related Cost	Average Range*
Civil Site Work	1 to 10%
Instrumentation	3 to 15%
Electrical Site Work	7 to 12%
Piping	5 to 12 %
Construction Contingency	10 to 35%
Engineering, Legal and Administrative	15 to 30%
Overall Project Risk	5 to 20%

* Average ranges based on experience with surface water treatment plant design.

If the MBfR is located in a remote area, the range of construction costs may be higher than the data presented in Table 3-4. For example, transportation and labor rates may be higher if labor and materials are not readily available in a remote location. However, we will assume that these are acceptable ranges for our final analysis.

Construction contingencies are often applied to the cost estimate to account for items not specifically included in a project scope but found to be necessary. The level of contingency selected should reflect the level of detail provided during pre-design. A low contingency budget reflects a high degree of confidence in the pre-design and a high contingency budget reflects a low level of confidence in the pre-design. A low degree of confidence may be due to limited availability of detailed costs or an experimental treatment technology. The recommended contingency levels for the varying types of cost estimates are listed in Table 3-5.

Table 3-5
Recommended Contingency for Corresponding Level of Estimate

Type of Cost Estimate	Level of Accuracy	Recommended Contingency
Order-of-Magnitude	+50% to –30%	20% to 30%
Conceptual	+40% to –20%	20% to 15%
Preliminary Design	+30% to –15%	15% to 10%
Definitive	+15% to –5%	10% to 5%

3.2.3 Calculations

From the data entered in the input section of the cost model, the construction and production costs can be calculated. Included in those calculations are:

- Design Data
- Cleaning Requirements
- Pumping Requirements
- Pre and Post Treatment Requirements

3.2.3.1 Design Data

Surface Area of Membrane Required. This number is based on the design flow rate, the perchlorate flux rate, and the difference between the influent and effluent perchlorate concentrations. Calculating the membrane surface area is critical as it is used to calculate the number of modules required for a given design flow rate and influent perchlorate concentration.

Total Number of Membrane Modules. This number is calculated by dividing the total membrane surface area by the membrane module surface area.

Packing Density per Module. The packing density is the number of fibers per module multiplied by the fiber cross sectional area, divided by the cross sectional area of the module. While the packing density does not effect the final treatment cost, it can effect the treatment efficiency. This number has been included in the calculated design information to let the user be aware of how dense each module will be packed. An upper limit warning pops up if the density exceeds 10%. A recommendation will be provided based pilot testing observations.

Calculated HRT. The hydraulic retention time (HRT) is calculated in this section to verify the theoretical HRT entered in the input section (and to compare with the actual HRT upon startup)

Building Square Footage. The building square footage is the footprint calculated from the sum of all equipment requiring enclosure. Once the facility footprint has been determined, the total square footage is multiplied by a unit cost of $150. This value is based on a one-story building and includes HVAC and lighting.

3.2.3.2 Cleaning Requirements

Pilot operation revealed that daily air scouring and monthly acid cleaning (citric acid) prevented excessive buildup of biomass within the MBfR modules. This section calculates the annual cleaning cost including compressed air requirements, chemical

costs, and associated chemical cleaning equipment (i.e. clean-in-place unit, chemical storage, compressors, etc.).

3.2.3.3 Pumping Requirements

This section calculates the required horsepower per pump per pump function (i.e. recirculation, backwashing, or final discharge). The horsepower requirements were calculated by:

$$\text{Horsepower} = \frac{r * Q * H}{550\ E}$$

Where r = Density of the fluid (water = 62.4)
Q = Flow rate (gpm)
H = Total head (feet)
E = Efficiency of pump (%)

A minimum of two pumps is recommended for all critical systems (i.e. recirculation, effluent, etc.). Based on design flow and recirculation rates, more pumps may be recommended to provide additional backup or system redundancy.

3.2.3.4 Pre- and Post-MBfR Treatment Requirements

This section contains optional treatment equipment and may be selected by the user in the input section of the cost model. For our analysis, the following options will be considered:

- Auto-backwashing strainer to remove suspended solids prior to entering the MBfR,
- Aeration requirements, and
- Post treatment filtering with multimedia filters

An auto-backwashing strainer is recommended as pretreatment to the MBfR for full-scale applications. A strainer would remove suspended solids prior to entering the MBfR and provide added protection to the system in the event of a raw water upset, such as high suspended solids. Aeration is recommended to provide dissolved oxygen (DO) to the treated water, as the system consumes DO during the treatment process. The multimedia filters are recommended to remove detached biomass that may discharge from the MBfR with the treated water

3.2.4 Cost Information

This subsection presents the construction and O&M cost categories that will be presented with the final analysis. Also included are the assumptions associated with these costs.

3.2.4.1 Construction

There are four main categories evaluated for full-scale design. The major categories affecting the constructed cost include:

- Equipment cost
- Construction cost
- Engineering, legal, construction management, and administrative costs
- Risk associated with an experimental technology

3.2.4.2 Assumptions Associated with Construction Costs

The following assumptions were made for the equipment and installation in the construction cost estimate (assumed included in cost):

- Membrane units are low pressure complete with all membrane modules, housings and all necessary equipment;
- Each membrane units contains its own feed or treated water flow or pressure control valves;
- Installation includes integrity testing at each unit;
- Interconnecting pipe work complete with all necessary flexibility and anti-vibration equipment;
- Control system and interface to existing or other control and telemetry systems;
- Motor control center (MCC) and distribution boards to supply all items of electrical plant - electrical system to include cabling, trays, trunking, accessories and supports between the membrane plant MCC, process control panel, motor drives and instrumentation;
- All necessary protective coatings and linings for plant;
- All ratings plates and labels;
- Feed and treated water quality instruments;
- Backwash holding tanks complete with fully automated duty/standby backwash pumps;
- Water softener(s) for use with caustic chemicals if required;
- All necessary trace heating and lagging;
- Filtrate (final effluent) feed pumps.

Not included with the equipment and installation are:

- Feed water pumps;
- Feed water balance tank(s);
- Filtrate water balance tank(s);

3.2.4.3 Operation and Maintenance

The operation and maintenance (O&M) costs associated with operating a new MBfR (whether a new plant or expansions to an existing plant) include:

- Maintenance Costs
- Cleaning Costs
- Energy Costs
- Hydrogen Costs
- Labor Costs

3.2.5 Financial Assessment

3.2.5.1 Present Worth Analysis

The present worth (present value) of the total capital costs to construct a MBfR plant, including the annual operation and maintenance needs, were evaluated by present worth analysis. The present worth of any value (such as the capital and O&M costs of the MBfR plant) is the equivalence of any future amount to the present amount. In this case it would be applied to the loan (or bond) estimate required to construct and operate the facility. The present worth is calculated by:

$$P = F(1+i)^{-n} = \frac{F}{(1+i)^n}$$

Where: P = Present value
$(1+i)^{-n}$ = Single payment present worth factor
F = Future Amount
i = Interest rate
n = Number of years

3.2.5.2 Amortization

If the loan to construct the MBfR plant is to be paid back in equal payments over the life of the loan, the loan is amortized. The amortized cost for the MBfR plant was calculated through the division of the total capital cost over the number of years of the life of a loan:

$$\text{Amortized Cost} = \frac{\text{Total Cost (\$)}}{\text{Number of Years}}$$

3.2.5.3 Water Production Cost

The water production cost is the cost per unit (i.e. per gallon, thousand gallons, acre-ft, etc.) to produce water. Understanding that preferences change between regions (including units) we will present our results both $/1000 gallons and $/acre-ft.

3.3 KINETICS OF PERCHLORATE REDUCTION

Researchers have shown that bioreactors can reduce perchlorate to below 4 µg/L when the initial concentration is high or when the reactor has been previously operated at high perchlorate concentrations (Kim and Logan 2000; Logan 2002; Giblin, Herman et al. 2000). However, low initial perchlorate concentrations, in the µg/L range, may preclude growth on perchlorate as the sole acceptor. Consider the biomass balance for batch growth:

$$\frac{dX}{dt} = q_{\max}\frac{S}{S+K}YX - bX$$

where S is the rate-limiting substrate concentration [M_S/L^3], q_{max} is the maximum specific substrate utilization rate [M_X/M_S-T], K is the half-maximum-substrate-utilization constant [M/L^3], X is the biomass concentration [M_X/L^3], Y is the biomass true yield [M_X/M_S], and b [1/T] is the endogenous decay rate. When S is small with respect to K, it can render the positive term on the right side of the equation smaller than the negative term, providing a net decay in biomass for any value of X. Under such conditions, biomass cannot be produced. S_{min} is the minimum concentration that can support steady-state biomass for a continuous suspended or biofilm system, and is calculated from

$$S_{\min} = \frac{Kb}{Yq_{\max} - b}$$ (Rittmann and McCarty 2001)

Fortunately, nitrate can serve as a primary electron-acceptor substrate, i.e., nitrate reduction can generate biomass that concurrently reduces perchlorate and nitrate. However, for a mixed-culture system, it is not clear whether nitrate reduction will result in perchlorate-reducing denitrifiers or common denitrifiers that cannot reduce perchlorate.

3.3.1 Batch Kinetic Test Conditions

Batch tests were carried out to determine the kinetic parameters q_{max}, Y, and K for *Dechloromonas* sp. PC1 (GenBank accession number AY126452), a novel, autotrophic, perchlorate-reducing bacterium previously isolated. The Y and q_{max} were determined using batch experiments with high initial acceptor and low initial biomass concentrations. The K was determined using batch non-growth tests with low initial biomass and acceptor concentrations. The experiments used 1-L bottles filled with 200 mL of media or 160 mL serum bottles filled with 25 mL of media, capped with butyl rubber stoppers, vacuum degassed, and filled with a gas mixture of 95% hydrogen and 5% CO_2 (for q_{max} and Y) or with pure hydrogen (for K). The bottles were shaken on their side at 200 rpm. The experiments were carried out at least in triplicate. The growth medium contained, per liter: 1.386 g Na_2HPO_4, 0.849 g KH_2PO_4, 0.1 g $(NH_4)_2SO_4$, 0.2 g $MgSO_4.7H_2O$, 1 mg $CaCl_2.2H_2O$, and 1 mg $FeSO_4.7H_2O$. The trace mineral solution is described in (Nerenberg, Rittmann et al. 2002). The K experiments were carried out in a 12-mM

phosphate buffer at pH of 7 with no nutrients or trace minerals. The pH was adjusted using 1 M NaOH for a final pH of 7.0. Curve fitting was used to estimate kinetic parameters q_{max} and K for PC1 using a finite-differences solution of the substrate-utilization and biomass-growth equations:

$$\frac{dS}{dt} = -\frac{q_{max} S}{S + K} X \text{, and}$$

$$\frac{dX}{dt} = \frac{Y q_{max} S}{S + K} X - bX .$$

These equations neglect competitive inhibition from chlorate during perchlorate reduction, so the q_{max} for perchlorate is an "apparent" value, valid only for the perchlorate range for which it was determined.

3.3.2 Strain PC1 Kinetic Parameters

Kinetics parameters were determined for *Dechloromonas* sp. PC1. Figure 3-16 shows a typical growth curve for PC1 on perchlorate and was used to estimate q and Y. The results from a typical K experiment are presented in Figure 3-17. Similar plots were obtained for nitrate.

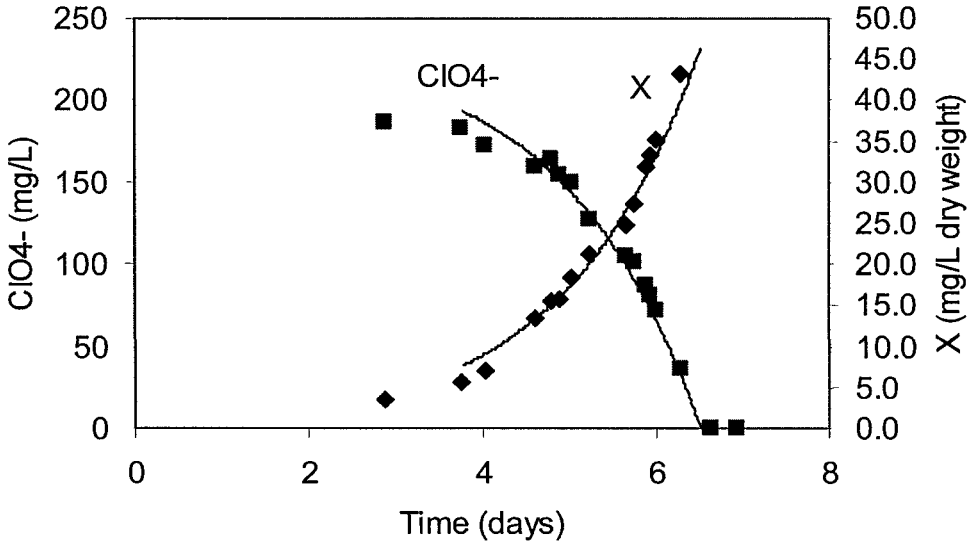


Figure 3-16
Estimation of q and Y (*Dechloromonas* sp. PC1)

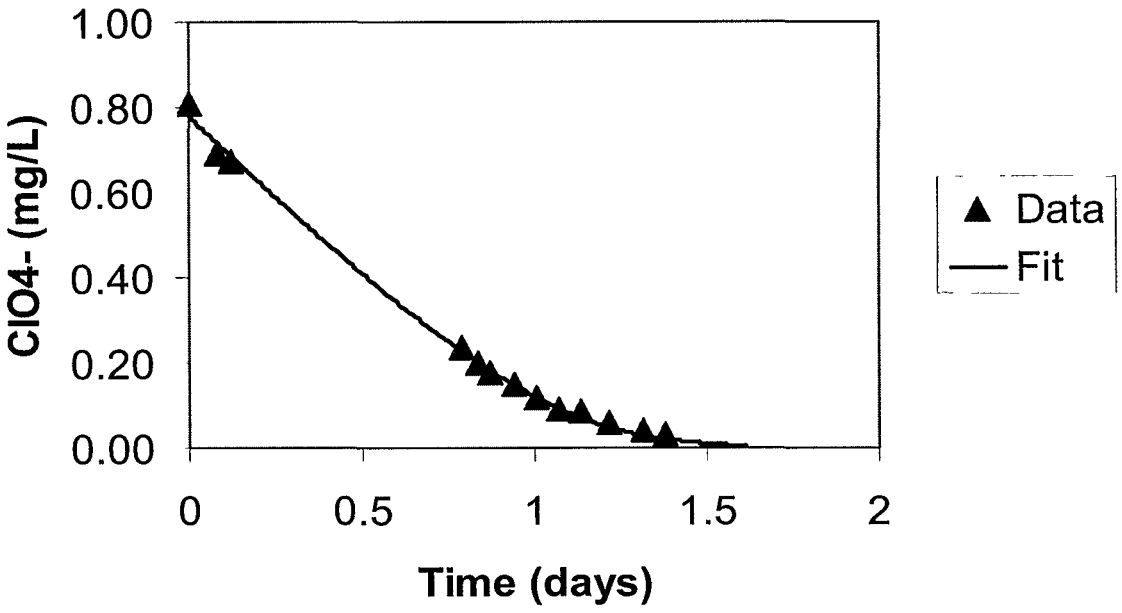


Figure 3-17
Estimation of K (*Dechloromonas* sp. PC1)

As shown in Table 2-5, the yields for perchlorate were very similar to those for nitrate. This is consistent with the similar Gibb's free energy at pH 7 ($\Delta G_o'$) for perchlorate and

nitrate reduction with hydrogen (118 and 112 kJ/eq $e^- H_2$, respectively). The q_{max} for nitrate reduction was around 6 times higher than for perchlorate, on an electron-equivalent (or hydrogen-accepting) basis. This makes growth on nitrate much faster that on perchlorate. The K value for perchlorate was 0.15 mg/L, two orders of magnitude lower than values from the literature for other perchlorate-reducing bacteria (Logan, Zhang et al. 2001).

Based on the kinetic parameters, the S_{min} for perchlorate is 40 µg/L. This is an approximate value, since q_{max} does not include competitive inhibition with chlorate. It is unlikely that the actual S_{min} would be much less than this value, therefore it is unlikely that perchlorate can be reduced to 4 µg/L with perchlorate as the sole electron acceptor.

Table 3-6
***Dechloromonas* sp. PC1 Kinetic Parameters**

S	q_{max} (eq $e^- H_2$/g X-day)	Y (gX/eq $e^- H_2$)	K (mg/L)	S_{min} (µg/L)
ClO_4^-	0.25	2.88	0.15	40
NO_3^-	1.43	2.46	<0.05	<2

Notes: (1) "eq $e^- H_2$" = equivalent of electrons from hydrogen; (2) 1 eq $e^- H_2$ = 1 g H_2; (3) b=0.1 1/day

3.4 REGULATORY APPROVAL

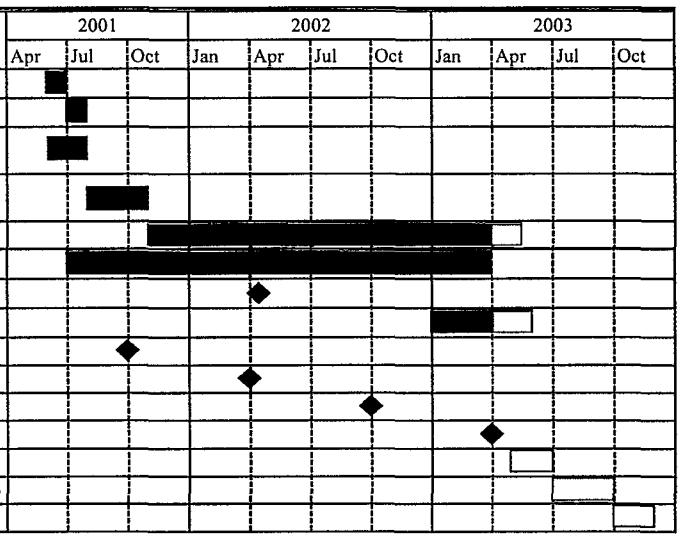
The project team has submitted documentation to the respective health departments of California, Utah, Texas, and Massachusetts, to ascertain those issues that need to be addressed before regulatory approval of the process for potable water production could be granted. A copy of the memo is included in the Appendix.

Chapter 4– Next Period Activities

4.1 SCHEDULE

The overall 23-month schedule for the project is shown in Figure 4-1. At this third progress report, the pilot testing is to be concluded in the following month and the draft final report will be submitted at the end of June after the PAC reviews this progress report.

ID	Task Name	Start	End
1	Develop Detailed Workplan	6/1/2001	6/29/2001
2	PAC Review of Plan	7/2/2001	7/20/2001
3	Refinement and Finalization of Pilot Plant Design	6/1/2001	8/1/2001
4	Construction and Installation of Pilot Plant	8/1/2001	10/1/2001
5	Pilot Plant Operation	9/24/2001	5/31/2003
6	Bench Testing at NWU	7/2/2001	4/1/2003
7	PAC Meeting	4/12/2002	
8	Data Analysis	2/3/2003	3/31/2003
9	First Progress Report	10/1/2001	
10	Second Progress Report	4/1/2002	
11	Third Progress Report	10/1/2002	
12	Fourth Progress Report	4/1/2003	
13	Draft Final Report	4/1/2003	6/1/2002
14	PAC Review of Draft Report	6/1/2003	10/1/2003
15	Final Report	10/1/2003	12/1/2003



■ Completed
□ To be completed

Figure 4-1
Project Schedule

Chapter 5 – Outreach Report

Members of the project team continue to disseminate the technical information that has been developed as a part of this project. Each of these efforts will acknowledge the financial and administrative support that has been provided by the AWWA Research Foundation and the U.S. Federal Government through the Environmental Protection Agency. They will also make sure that it is clear that the information presented is based on the views of the project team and not of AWWA Research Foundation or the U.S. Federal Government.

The following papers and presentations have been given:

- G. Lehman, S. Adham, T. Gillogly, B. Rittman (2003). Removal of Perchlorate using Hydrogen-Fed Membrane Biofilm Reactors. American Water Works Association Membrane Conference. Atlanta, Georgia.

- T. Gillogly, G. Lehman, S. Adham, R. Nerenberg and B. Rittmann (2002). East Valley Water District Conference on Perchlorate. Ontario, CA. (October 2002).

- S. Adham, T. Gillogly, G. Lehman, R. Nerenberg, B. Rittmann, R. Nerenberg (2002) Removal of perchlorate with membrane biofilm reactors. Water Quality Technology Conference. Seattle, WA.

The following abstracts were accepted for upcoming conferences:

- S. Adham, T. Gillogly, G. Lehman, B. Rittmann, R. Nerenberg (2003). Membrane Biofilm Reactors for Removal of Perchlorate. American Water Works Association ACE. Anaheim, California (June 2003).

- B. Rittmann, R. Nerenberg, T. Gillogly, G. Lehman, S. Adham. Perchlorate reduction using the Hollow-Fiber Membrane Biofilm Reactor. 2003 Seventh Annual In Situ and On-Site Bioremediation Symposium. Orlando, FL (June 2003).

The following abstracts were submitted for upcoming conferences:

- G. Lehman, S. Adham, T. Gillogly, B. Rittmann, R. Nerenberg (2003). Removal of Perchlorate using Novel Hydrogen-Fed Biofilm Reactors. American Water Works Association CA/NV Section. San Diego, California (June 2003).

- S. Adham, T. Gillogly, G. Lehman, R. Nerenberg, B. Rittmann, R. Nerenberg (2003) Removal of perchlorate with membrane biofilm reactors. Water Quality Technology Conference. Seattle, WA.

Chapter 6 – Appendix

MWH

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Subject: Review of an Innovative Perchlorate Treatment Technology

Dear NAME

MWH is currently involved in the pilot-scale demonstration of an innovative perchlorate treatment technology as a part of an American Water Works Association Research Foundation grant. We would appreciate if you would review the enclosed information and return any comments or concerns that should be addressed prior to MWH requesting a formal acceptance of the technology for the production of potable water.

BACKGROUND

Since the detection of perchlorate in some California groundwaters in early 1997, several studies have evaluated multiple treatment technologies for its removal. Three treatment technologies have proven to be technically feasible at drinking-water treatment scale: biological reduction, ion-exchange, and reverse osmosis (RO) membranes. Although ion exchange and RO are proven technologies for water treatment, they only concentrate perchlorate into waste streams that require further disposal and/or treatment. On the other hand, biological reduction reduces perchlorate to the innocuous chloride ion (Cl^-) without the production of any residuals that require special handling, which is a major advantage.

PROCESS DESCRIPTION

Numerous approaches and process configurations have been utilized to develop a biologically reductive system. The system presented herein centers around a novel membrane biofilm reactor (MBfR). This reactor contains hollow-fiber membranes potted at both ends of the cylindrical module. Hydrogen is fed to one end of the reactor, filling the inside of the fibers and passively diffuses through the membranes to serve as an electron donor for the biofilm that grows on the outside of the hollow-fibers, as shown in Figure 1. The biofilm within the reactor developed from indigenous bacteria already present in the groundwater and was not artificially inoculated or amended.

It is important to note that the purpose of the membrane hollow-fibers is to provide a safe hydrogen delivery system and serve as a biofilm support media. Water does not pass through the hydrophobic membrane. The perchlorate-contaminated water is treated as it passes along the biofilm on the outside of the fibers. Within the hollow-fibers, the

hydrogen pressure is maintained below the bubble-point of the membrane, eliminating the formation of a hydrogen atmosphere within the bioreactor.

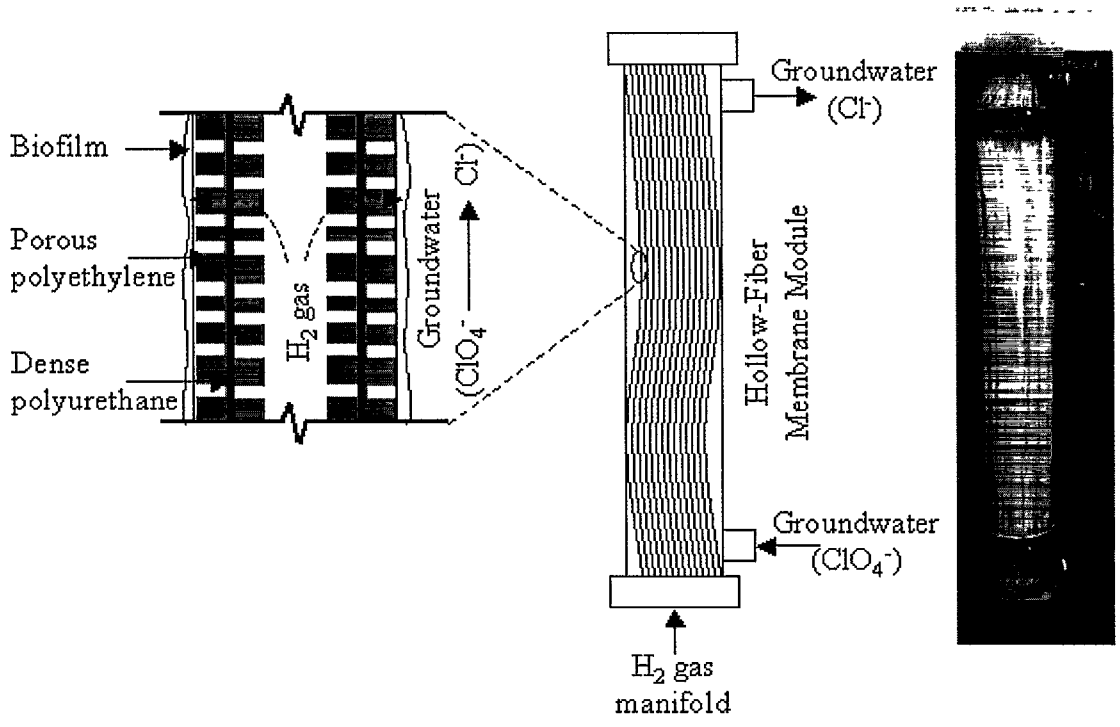

Figure 1
Membrane Biofilm Reactor (MBfR)

Hydrogen has four major advantages as an added electron donor. First, it is the least expensive donor per equivalent of electrons supplied. Second, it is non-toxic to humans. Third, it evolves from water that has an open surface, thereby eliminating a residual that could cause biological instability or disinfection byproducts in drinking water. Finally, it supports the growth of autotrophic bacteria, which form minimal excess biomass and need no organic carbon source that can form by-products.

While perchlorate and other electron acceptors (i.e. oxygen, nitrate), are reduced in the MBfR, additional processes were necessary to complete the pilot-scale treatment system. Following the MBfR, an aeration process is used to achieve two primary goals: first, it oxygenates the water in preparation for its introduction into a distribution system as a drinking water source; and second, it provides sufficient oxygen for operating the downstream media filter in an aerobic biodegradation mode to removal any residual aerobically degradable compounds.

While aerobic activity is important in the media filter, its primary role is to remove any biomass that may slough off during operation of the MBfR. (Excess biomass within the MBfR itself is regularly removed by air scour. This biomass-laden water, however, is directed to waste and is not allowed to pass onto the media filters.) In a full-scale operation, the media filter effluent would then be dosed with chlorine to provide disinfection and carry a residual through the distribution system. Alternatively, media

filtration could be replaced by membrane filtration for increased protection against the breakthrough of sloughed biomass.

PROCESS PERFORMANCE

Perchlorate Reduction

The MBfR process has been demonstrated at pilot-scale to consistently reduce perchlorate contaminated groundwater[1] (55 µg/L) to below the current 4 µg/L California Department of Health Services (CaDHS) perchlorate action limit. In addition, simultaneous removal of influent dissolved oxygen and nitrate to below detection limits was observed (summarized in Table 1). The removal rates have been observed with the MBfR system operated at a system flow rates corresponding to theoretical hydraulic residence times between 7 and 30 minutes. In addition, the water within the reactor was recycled to achieve an average linear fluid velocity of 100 cm/min (1.7 cm/sec) through the reactor.

Table 1
Reduction of Oxygen, Nitrate and Perchlorate

Parameter	Influent	Effluent	Removal Efficiency
Perchlorate	55 µg/L	2 µg/L	96%
Nitrate	6 mg-N/L	<0.02 mg-N/L	>97 %
DO	8.1 mg/L	<0.10 mg/L	>99 %

Hydrogen Consumption

In contrast to many biological processes in which the electron donor is supplied to the bulk fluid and then must diffuse from the bulk fluid to the biofilm, hydrogen is fed directly to the biofilm. Consequently, excess hydrogen dosing can be tightly controlled. The system is operated such that a hydrogen residual of approximately 0.15 mg/L is maintained in the reactor effluent.

Throughout the course of recent pilot-testing, the hydrogen consumption was monitored. Based on the mass of oxygen, nitrate, and perchlorate that had been reduced the stoichiometric consumption of hydrogen was calculated, as shown in Table 2. Figure 2 is a summary of hydrogen consumption observed during three critical stages of the pilot testing: during startup, the biofilm development state, and steady-state growth. During all three stages, a high degree of correlation was observed between the hydrogen consumption calculated from pilot-scale process measurements and the predicted theoretical consumption.

[1] The groundwater is drawn from an active well owned and operated by the La Puente County Water District located in Baldwin Park, California.

Table 2
Theoretical Hydrogen Consumption

Reactant	Half-Reaction	H_2 Consumption†
Oxygen	$O_2 + 2H_2 \rightarrow 2H_2O$	139 µg H_2 / mg O_2
Nitrate	$2NO_3^- + 5H_2 + 2H^+ \rightarrow N_2 + 6H_2O$	396 µg H_2 / mg NO_3^--N
Perchlorate	$ClO_4^- + 4H_2 \rightarrow Cl^- + 4H_2O$	0.0892 µg H_2 / µg ClO_4^-

† - The stoichiometric H_2 consumption has been increased by 10 percent to account for biomass production.

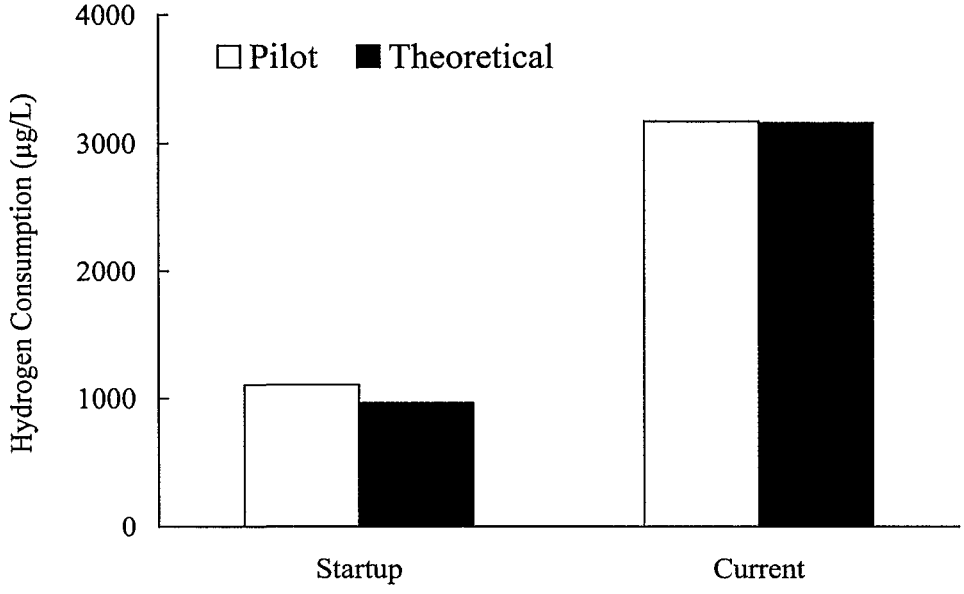

Figure 2
Hydrogen Utilization

Water Quality

An extensive sampling campaign was performed to characterize water quality through of the entire pilot-scale treatment process. All treated effluent water quality parameters were found to be in compliance with both the National Primary Drinking Water Standards and Secondary Drinking Water Regulations. Additional analyses were performed to determine if other compounds were either reduced or produced through the treatment train. These additional analyses included: SVOCs, VOCs, aldehydes, aldicarbs, diquat/paraquat, TOC and HPCs. As listed in Table 1, the only significant changes were detected in the HPCs. As expected high concentrations of bacteria were measured in the effluent of this biological treatment process. However, dosing preformed chloramines (2.5 mg/L) was sufficient to reduce the HPCs to zero.

Table 1
Summary of MBfR Process Treated Water Quality

Parameter	Method	Comment
National Primary Drinking Water Standards	Various	In Compliance
National Secondary Drinking Water Regulations	Various	In Compliance
Additional Testing		
Semivolatiles	ML/EPA 525.2	ND
Regulated VOCs	ML/EPA 524.2	ND
Aldicarbs	ML/EPA 531.1	ND
Diquat / Paraquat	ML/EPA 549.2	ND
HPCs	SM 9215B	Raw water (1600 CFU/mL) MBfR Effluent (>5700 CFU/mL) Media Filter Effluent (>5700 CFU/mL) Post-Cl_2 Addition (2.5 mg/L NH_2Cl; 0 CFU/mL)
TOC	SM 9215B	Raw water (<0.5 mg/L) MBfR Effluent (0.6 mg/L) Media Filter Effluent (<0.5 mg/L) Post-Cl_2 Addition (<0.5 mg/L)

Operation & Maintenance

During long-term operation, it was determined that the reactors must be cleaned to maintain their effectiveness. Without cleaning several problems may develop including:

- *Excess Biomass*. The build-up of excess biomass can lead to the clumping of fibers, which reduces the effective biofilm area, exacerbates short-circuiting, reduces mass transport of perchlorate to reductive organisms in the biofilm, and increases the distance hydrogen must diffuse to reach the outer portion of the biofilm. Each of these can result in decreased performance of the system.

- *Sulfate Reduction*. If the biomass is not regularly exposed to oxygen and excess biomass is not frequently removed (i.e. slow growing organisms are allowed to proliferate), sulfate-reducing organisms may establish themselves in the biofilm. Once established, the reduction of sulfate and concomitant production of hydrogen sulfide will result in a mild aesthetic problem. However, the subsequent aeration and chlorination processes oxidize any residual concentration of sulfide to sulfate.

- *Calcification*. Over time calcium carbonate can precipitate on the walls of the reactor and deposit within the biofilm. If the calcium carbonate in the biofilm is not regularly displaced, it can accumulate leading to the calcification of the fibers. Calcification of the fibers reduces their flexibility and can result in fiber breakage when the hydraulics through the reactor change with varying flow rates or air scour. It can also result in decreased hydrogen transfer if the calcium precipitates within the pores of the fiber.

- *Fiber Breakage.* In contrast to traditional membrane filtration processes, a compromised fiber in the MBfR does not impair the finished water quality. It does, however, allow water to pass back into the lumens decreasing hydrogen transfer. It is this apparent "condensation" that is detectable that indicate when a fiber has been compromised. Repair of the compromised fiber is accomplished sealing the ends of the compromised fiber, similar to traditional membrane filtration processes.

Regular air scour (daily or every other day) can effectively mitigate the accumulation of excess biomass, development of a sulfate reducing environment, and calcification of fibers. As the bubbles from the air scour are created and rise through the membrane fibers, they create turbulence, stripping loosely attached biomass from the fibers. The oxygen introduced during air scour also inhibits the growth of sulfate reducing bacteria. Additionally, calcium measurements of the scoured biomass indicate that the calcium precipitates in the biofilm and consequently, is removed during air scour.

While the air scouring is an effective regular cleaning process, periodic cleanings that are more rigorous in nature are recommended to regulate calcification in "difficult to air scour" areas. The rigorous cleaning process utilized the application of a 3 percent citric acid solution to clean the membranes. The membranes were soaked in this solution for one hour with recycle, to ensure that all regions of the reactor were uniformly treated, and then rinsed with clean water before being returned to service.

It is important to note that despite the apparent rigors of either air scour, mild acid cleaning, or periodic process interruptions (source water interruption, pump maintenance, etc.), system was able to quickly return to normal performance (>95 percent reduction of perchlorate) within three hydraulic retention times, demonstrating a surprisingly roust biofilm process. If, however, the system undergoes rigorous acid cleaning the biofilm must be redeveloped. Traditionally, biofilm redevelopment typically takes 3 to 5 days.

SUMMARY

The innovative MBfR process has the potential to treat a variety of oxidized contaminants. Results obtained from the pilot plant show the successful removal of perchlorate from a contaminated southern California groundwater. We feel that this technology is potentially applicable to many of the water supplied impacted by perchlorate. With your help, we would like to explore the regulatory issues that would need to be addressed for approval of this technology.

We appreciate you taking the time to review this material and look forward to your response. Please do not hesitate to contact me should you have any questions (626-568-6005; samer.adham@mwhglobal.com).

Sincerely,

Samer

Samer Adham, Ph.D.
Principal Investigator

CC: Thomas Gillogly, Ph.D.
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